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# Alkylation of Nitriles with Gaseous Carbenium Ions. The Ritter Reaction in the Dilute Gas State

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**Abstract:** Radiolytically formed carbenium ions, such as *sec*-$C_3H_7^+$, *sec*-$C_4H_9^+$, and *t*-$C_4H_9^+$, react in the gas phase with model aliphatic and aromatic nitriles yielding the corresponding nitrilium ions. The latter undergo efficient condensation with water that eventually leads to the formation of the corresponding *N*-alkylamides. The mechanism is analogous to the Ritter reaction in solution. The reactivity and selectivity of the gas-phase electrophilic attack on nitriles has been deduced from competition experiments under conditions that largely exclude the effects of solvation, ion pairing, etc., which complicate the interpretation of solution-chemistry measurements.

In recent years, radiolytic techniques have been applied to the study of the structural and mechanistic aspects of ion-molecule reactions occurring in the dilute gas state.[2] In particular, attention has been focused on the reactivity of gaseous carbenium ions with various nucleophiles which has resulted in (i) the demonstration of actual bond formation between the electrophilic carbon and *n*-donor atoms of the substrate and (ii) the measurement of the branching ratio of the energetically allowed reaction channels (i.e., proton transfer vs. alkylation).[3-10]

The determination of the protonation site of HCN and $CH_3CN$, a problem closely related to the subject of this study, has recently been investigated by various mass-spectrometric techniques that include flowing afterglow,[11] ICR,[12] pulsed high-pressure,[13] and collisional activation.[14] The results support the view of a predominant proton transfer to the nitrogen atom of the substrate, which is also in agreement with CI and SCF calculations.[15] However, the evidence provided by mass spectrometric techniques is rather indirect. For example, Meot-Ner has used admittedly qualitative thermochemical arguments to assign the protonated isocyanide structure to the charged intermediates from the addition of *sec*-$C_3H_7^+$ and *t*-$C_4H_9^+$ to HCN.[13]

In the present work, we examine the addition reaction of *sec*-$C_3H_7^+$, *sec*-$C_4H_9^+$, and *t*-$C_4H_9^+$ ions, obtained from the $\gamma$ radiolysis of suitable alkanes, with gaseous $CH_3CN$ and $C_6H_5CN$. Our goals are to obtain direct evidence for the predominant reactivity of the nitrogen atom in model nitriles and to assess their relative reaction rate toward gaseous carbenium ions.

## Experimental Section

**Materials.** The gaseous hydrocarbons employed, isobutane, 2,2-dimethylpropane, propane, and *n*-butane, were research-grade reagents from Matheson Co., $O_2$ and $NH_3$ were locally purchased research-grade gases. Benzene and toluene were gas chromatographic standards from C. Erba Co. Acetonitrile and propionitrile from Merck AG. and benzonitrile from C. Erba Co. were analytical-grade reagents redistilled with a spinning band column to get a purity exceeding 99.9 mol %, as checked by GLC. The *N*-alkylamides, used for identification or calibration purposes, were prepared by reacting the corresponding alkylamines with acyl chlorides in diethyl ether solution. Their identity was confirmed by mass spectrometry and by IR and NMR spectroscopy.

**Procedure.** The experimental techniques employed for the preparation and the irradiation of the gaseous systems in 500-mL pyrex ampules were previously described.[16] The irradiations were carried out at 30 °C in a 220 Gammacell (Nuclear Canada Ltd.) at a dose rate of ca. 0.43 Mrad $h^{-1}$ to a total dose of 2.2 Mrad, as measured with a Fricke dosimeter. Control experiments demonstrated that the relative yields of products are largely independent of the radiation dose—at least up to 17 Mrad.

The content of the irradiated vessels were extracted with methanol, or diethyl ether, and analyzed by GLC on a Sigma 1 gas chromatograph from Perkin-Elmer Co., equipped with a FID unit, using the following columns: (i) a 12 m or a 50 m × 0.02 mm i.d. fused-silica capillary column, coated with methyl silicone (SP 2100) and operated with a temperature program from 55 to 100 °C and from 95 to 250 °C, respectively, and (ii) a 2 m × 2 mm i.d. glass column filled with 3% Carbowax 20M on 100/120 mesh Chromosorb HP-DMCS and operated with a temperature program from 40 to 205 °C.

The products were identified by comparison of their retention volumes with those of authentic samples. Their yields were deduced from the area of the corresponding elution peaks that were individually corrected for the detector response. The identity of the products was further confirmed by GL-MS with a Hewlett-Packard Model 5982A mass spectrometer, operating in the EI or the CI mode. The same instrument was employed in preliminary chemical ionization experiments for selecting the appropriate composition of the gaseous system in the radiolytic runs.

## Results

The yields of the products from the reaction of radiolytically formed alkyl cations with the nitriles in the presence of water vapor, used as a trapping reagent for the charged intermediates, are given in Table I. The $G_{(+M)}$ values listed should be taken only as a crude estimate (within 30%) of the *absolute yields* of the products, owing to the large experimental errors affecting the measurement of the actual radiation dose absorbed by the gaseous systems. Nevertheless, these figures are instrumental in showing that the compounds isolated from the reaction are really major ionic products, by comparison with the known $G_{(R^+)}$ values for the formation of the alkyl cations from the radiolysis of the parent hydrocarbons.[17] In addition, the experimental data display an

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Table I. Products from the Gas-Phase Reaction of Alkyl Cations with the Nitriles in the Presence of Water Vapor

| system composition (torr)[a] | | | | | yield of product(s) [$G_{(M)}$] from substrate A and B | | apparent rel reaction rates $k_A/k_B$ |
|---|---|---|---|---|---|---|---|
| | | substrate | | | | | |
| reagent gas | $H_2O$ | A | B | reactant ion | A | B | |
| $i$-$C_4H_{10}$, 710 | <1.5 | $CH_3CN$, 3.0 | | $t$-$C_4H_9^+$ | $CH_3CONH$-$t$-$C_4H_9$, 2.6 | | |
| 700 | 15.2 | $CH_3CN$, 3.0 | | $t$-$C_4H_9^+$ | $CH_3CONH$-$t$-$C_4H_9$, 1.2 | | |
| $neo$-$C_5H_{12}$, 704 | 2.4 | $CH_3CN$, 3.9 | | $t$-$C_4H_9^+$ | $CH_3CONH$-$t$-$C_4H_9$, 2.7 | | |
| 704 | 4.1 | $CH_3CN$, 2.2 | | $t$-$C_4H_9^+$ | $CH_3CONH$-$t$-$C_4H_9$, 2.3 | | |
| 700 | 4.8 | $C_6H_5CN$, 0.7 | | $t$-$C_4H_9^+$ | $C_6H_5CONH$-$t$-$C_4H_9$, 0.7 | | |
| 700 | 5.2 | $CH_3CN$, 1.5 | $C_7H_8$, 1.2 | $t$-$C_4H_9^+$ | $CH_3CONH$-$t$-$C_4H_9$, 0.9 | *tert*-butyltoluenes,[b] 0.1 | 6.8 |
| 700 | 5.9 | $C_6H_5CN$, 0.5 | $C_7H_8$, 1.0 | $t$-$C_4H_9^+$ | $C_6H_5CONH$-$t$-$C_4H_9$, 0.5 | *tert*-butyltoluenes,[b] 0.1 | 6.3 |
| 704 | 4.4 | $C_6H_5CN$, 0.6 | $CH_3CN$, 1.4 | $t$-$C_4H_9^+$ | $C_6H_5CONH$-$t$-$C_4H_9$, 0.3 | $CH_3CONH$-$t$-$C_4H_9$, 0.9 | 0.7 |
| 700 | 6.9 | $C_6H_5CN$, 0.6 | $CH_3CN$, 2.1 | $t$-$C_4H_9^+$ | $C_6H_5CONH$-$t$-$C_4H_9$, 0.3 | $CH_3CONH$-$t$-$C_4H_9$, 1.1 | 0.9 |
| $C_3H_8$, 700 | 5.4 | $CH_3CN$, 4.3 | | $sec$-$C_3H_7^+$ | $CH_3CONH$-$sec$-$C_3H_7$, 1.2 | | |
| 704 | 4.5 | $CH_3CN$, 2.2 | | $sec$-$C_3H_7^+$ | $CH_3CONH$-$sec$-$C_3H_7$, 0.9 | | |
| 704 | 2.6 | $C_2H_5CN$, 1.8 | | $sec$-$C_3H_7^+$ | $C_2H_5CONH$-$sec$-$C_3H_7$, 1.0 | | |
| 706 | 3.4 | $C_6H_5CN$, 0.4 | | $sec$-$C_3H_7^+$ | $C_6H_5CONH$-$sec$-$C_3H_7$, 0.1 | | |
| 705 | 3.9 | $CH_3CN$, 1.1 | $C_6H_6$, 1.0 | $sec$-$C_3H_7^+$ | $CH_3CONH$-$sec$-$C_3H_7$, 0.6 | cumene, 0.3 | 2.0 |
| 706 | 3.1 | $C_6H_5CN$, 0.7 | $C_6H_6$, 1.5 | $sec$-$C_3H_7^+$ | $C_6H_5CONH$-$sec$-$C_3H_7$, 0.3 | cumene, 0.7 | 0.8 |
| 704 | 3.2 | $C_6H_5CN$, 0.7 | $CH_3CN$, 2.2 | $sec$-$C_3H_7^+$ | $C_6H_5CONH$-$sec$-$C_3H_7$, 0.2 | $CH_3CONH$-$sec$-$C_3H_7$, 0.9 | 0.5 |
| $n$-$C_4H_{10}$, 704 | 3.2 | $CH_3CN$, 1.9 | | $sec$-$C_4H_9^+$ | $CH_3CONH$-$sec$-$C_4H_9$, 0.9 | | |
| 704 | 3.3 | $C_6H_5CN$, 0.7 | | $sec$-$C_4H_9^+$ | $C_6H_5CONH$-$sec$-$C_4H_9$, 0.1 | | |
| 704 | 2.5 | $CH_3CN$, 1.9 | $C_7H_8$, 1.1 | $sec$-$C_4H_9^+$ | $CH_3CONH$-$sec$-$C_4H_9$, 1.3 | *sec*-butyltoluenes,[c] 0.3 | 2.5 |
| 704 | 2.1 | $C_6H_5CN$, 0.6 | $CH_3CN$, 2.0 | $sec$-$C_4H_9^+$ | $C_6H_5$-$CONH$-$sec$-$C_4H_9$, 0.06 | $CH_3CONH$-$sec$-$C_4H_9$, 0.8 | 0.3 |

[a] All the systems contained 10 torr of $O_2$, in addition to the listed components. [b] Isomeric composition of *tert*-butyltoluenes = 6% meta, 94% para. [c] Isomeric composition of *sec*-butyltoluenes = 43% ortho, 30% meta, 27% para.

excellent internal consistency, with typical standard deviations well below 10%, and therefore allow an accurate evaluation of the *relative* product yields.

The significant features of the experimental results follow:

(i) The major product is invariably the *N*-alkylacetamide (benzamide) from the alkylation of acetonitrile (benzonitrile) by the carbenium ions formed from the radiolysis of the bulk component of the system. Thus, *N*-isopropylamides are obtained from $C_3H_8$, *N*-*sec*-butylamides from $n$-$C_4H_{10}$, and *N*-*tert*-butylamides from isobutane or neopentane. The alkylamides represent more than 80% of the overall product yields. They are accompanied by minor amounts of other alkylamides from the reactions of the other carbocations which are known to be formed in minor yields from the radiolysis of the various alkanes.[17] The reaction of $C_2H_5CN$ with isopropyl ions is exactly analogous to that of $CH_3CN$. No alkylation of the aromatic ring of benzonitrile has been observed which is compatible with the strongly deactivating properties of the cyano group.

(ii) The $G_{(R^+)}$ values for the formation of the carbenium ions from the $\gamma$ radiolysis of the appropriate hydrocarbon are approximately the same, i.e., in the range from 3 to 4. This allows an estimate of the *absolute* yields of the isolated products. Thus, comparison of the $G_{(+M)}$ values for the *N*-alkylamides with the known[17] $G_{(R^+)}$ values for the appropriate carbenium ions leads to the following absolute yields: *N*-*tert*-butylacetamide, ca. 70%, *N*-*sec*-propylacetamide, ca. 30%, *N*-*sec*-butylacetamide, ca. 25%. These values refer to gaseous systems characterized by a $[CH_3CN]:[H_2O]$ ratio from 0.5 to 0.6. Considerably lower $[C_6H_5CN]:[H_2O]$ ratios, typically in the range 0.1–0.2, must be used in the systems containing benzonitrile, due to the lower vapor pressure of the substrate. Correspondingly, lower absolute yields of amides were obtained, ca. 20% for *N*-*tert*-butylbenzamide, ca. 4% for *N*-*sec*-propylbenzamide, and ca. 3% for *N*-*sec*-butylbenzamide.

The yields of alkylamides drop at higher relative concentrations of $H_2O$, which was to be expected owing to the ability of the latter to compete with the nitrile for the carbenium ions (vide infra). The effect is much more pronounced in the case of the secondary cations then in the case of $t$-$C_4H_9^+$, where a tenfold increase of the $[H_2O]:[CH_3CN]$ ratio just roughly halves the yield of *N*-*tert*-butylacetamide formed. On the other hand, high yields of amides are obtained even at very low concentrations of water, indicating that trapping of the nitrilium ions from the addition of the carbenium ions to the nitriles is not rate limiting.

(iii) Competition experiments, involving benzene and toluene as the reference substrates respectively in isopropylation and butylation, indicate a relatively high stubstrate selectivity, the $k_{CH_3CN}/k_{C_7H_8}$ ratio being 6.8 in tert-butylation and 2.5 in sec-butylation, while the $k_{CH_3CN}/k_{C_6H_6}$ ratio is 2.0 in isopropylation. The $k_{C_6H_5CN}/k_{C_7H_8}$ value is 6.3 in tert-butylation, in contrast with the apparent lack of selectivity displayed by the *sec*-butyl cation ($k_{C_6H_5CN}/k_{C_7H_8} \simeq 0.8$) and the *sec*-propyl cation ($k_{C_6H_5CN}/k_{C_6H_6} \simeq 0.8$). Direct competition experiments between pairs of nitriles were carried out. The results confirm the higher reactivity of the aliphatic nitriles with respect to benzonitrile. A first-order dependence of the reaction rates on the concentration of the substrates was assumed in all cases.

Additional experiments were performed to ascertain whether acetamide (or benzamide) from the reaction of any protonated nitriles with water vapor could be isolated. To this end, gaseous mixtures, containing $H_2$ (720 torr), $O_2$ as a radical scavenger (10 torr), and traces of acetonitrile (or benzonitrile) and water in the molar ratio from 0.2 to 3.8 were irradiated.

Both $H_3^+$, from the radiolysis of the bulk constituent of the gas, and $H_3O^+$, from the protonation of water, were expected to undergo exothermic proton transfer to the nitriles. However, no acetamide (or benzamide) could be detected among the neutral products. From the detection limit of the analytical technique employed, it can be concluded that formation of $CH_3CONH_2$ ($C_6H_5CONH_2$) must occur, if at all, with very low yields, corresponding to $G_{(+M)}$ values below $10^{-2}$.

Chemical ionization mass spectra of isobutane and propane, containing 0.1 mol % nitriles, were recorded under a total pressure of ca. 1 torr. Formation of the $(M + C_4H_9)^+$ adduct ions could be detected in the isobutane spectra, while only protonated species, $(M + H)^+$, were formed in the mixtures containing propane.

## Discussion

**The Charged Reagents.** As a result of detailed mass spectrometric and radiolytic investigations,[17,18] the nature and yields of the carbenium ions from the irradiation of the alkanes used in the present study are well defined. Consequently, $sec$-$C_3H_7^+$, $sec$-$C_4H_9^+$, and $t$-$C_4H_9^+$ are known to be, by far, the major ionic species formed from propane, butane, and isobutane (or neopentane), respectively. This occurs either directly, e.g.

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(18) Cacace, F.; Ciranni, G.; Giacomello, P. *J. Am. Chem. Soc.* **1981**, *103*, 1513–1516.

$$C_3H_8 \rightsquigarrow C_3H_7^+ + H + e \qquad (1a)$$

$$C_3H_8 \rightsquigarrow C_2H_5^+ + CH_3 + e \qquad (1b)$$

or via fast, exothermic hydride-ion abstraction from the parent hydrocarbon by the fragment ions, e.g.

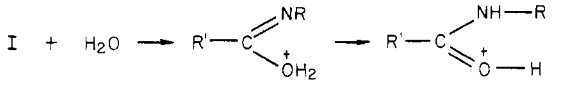
$$C_2H_5^+ + C_3H_8 \rightarrow C_2H_6 + C_3H_7^+ \qquad (2)$$

The composition of the irradiated systems, containing a large excess of the alkane and only traces of the nitrile(s), minimizes the direct radiolysis of the substrate. Furthermore, the carbenium ions from processes 1 and 2 must undergo a large number of unreactive collisions with the parent molecules before a reactive encounter with nitrile(s) can occur. Consequently, prior to reaction any excited ion from the radiolysis in the large excess of unreactive alkane can be expected to be effectively thermalized. Finally, the contribution of radical processes to the yield of the neutral end products can be expected to be suppressed by the appreciable concentration of $O_2$, being an excellent thermal radical scavenger. The ionic nature of the reactions responsible for the formation of the products is further confirmed by the marked decrease of the yields caused by addition of a few torr of $NH_3$, which is a known carbenium ion interceptor. In conclusion, it can be reasonably assumed that the formation of the isolated products can be traced to the attack of structurally well defined, thermal carbenium ions on the nitrile molecules.

**The Alkylation Process.** The predominant formation of *N*-alkylamides from all systems investigated can be traced to the primary attack of the carbenium ions on the nitrogen atom of the substrate. This leads to the formation of the corresponding nitrilium ion:

$$R^+ + R'CN \rightarrow R'\text{—}^+\underset{\mathrm{I}}{C}{\equiv}N\text{—}R \qquad (3)$$

Nitrilium ions (I) react subsequently with water, yielding intermediates which tautomerize to the protonated alkylamide structure,



(4)

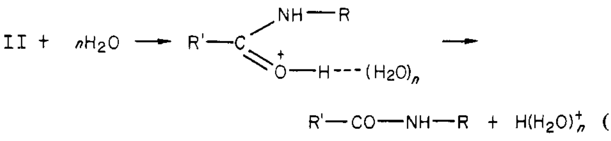
II

The relative alkylation rate of the substrates is largely independent of the water concentration, suggesting that (4) is a fast, non-rate-determining process.

Eventually II undergoes deprotonation with a sufficiently strong base to yield *N*-alkylamides, which are the major neutral products isolated:

$$\mathrm{II} + B \rightarrow R'\text{—CO—NH—}R + BH^+ \qquad (5)$$

In view of the high proton affinity (PA) of *N*-substituted amides[19] (probably the strongest bases present in the gas), it is likely that the deprotonation, and possibly the tautomerization step, require a cooperative process involving clustering of several water molecules, i.e.



(5a)

Isolation of *N*-substituted amides indicates that the gaseous electrophile selectively attacks the nitrogen atom of the substrate, yielding the nitrilium ion I as the primary alkylation product. Thus, the present results provide direct experimental evidence that supports earlier thermochemical arguments,[13] suggesting that the adduct ions observed in a low-pressure mass-spectrometric study of the reaction between carbenium ions and HCN have the isocyanide structure.

Unfortunately, thermochemical data necessary to evaluate the heat of formation of the nitrilium ions I are currently not available. Nevertheless, comparison with the known $\Delta H°$ values for the addition of *sec*-$C_3H_7^+$ and *t*-$C_4H_9^+$ to HCN, −30.8 and −16.3 Kcal $mol^{-1}$, respectively,[13] shows that reaction 3 must be appreciably exothermic for all substrates.

**Protonation vs. Alkylation.** Proton transfer from *sec*-$C_3H_7^+$ and *sec*-$C_4H_9^+$ to acetonitrile,

$$C_nH_{2n+1}^+ + CH_3CN \rightarrow C_nH_{2n} + CH_3CNH^+ \qquad (6)$$

is known[20] to be exoergic, the $\Delta G°$ values being respectively −6.7 and −6.8 kcal $mol^{-1}$. In contrast, proton transfer from *t*-$C_4H_9^+$ to acetonitrile is *endoergic* by 6.5 kcal $mol^{-1}$.

The explanation of the considerably lower alkylation yields from secondary carbocations, when compared to *t*-$C_4H_9^+$, could come from the operation of a proton-transfer channel competing with alkylation, allowed only for the chemical ionization spectra of acetonitrile, measured under the same pressure (ca. 1 torr) with propane or isobutane as the reagent gas. The abundant $(M + H)^+$ adduct ion present in the propane spectra is replaced by the $(M + C_4H_9)^+$ ion in the isobutane spectra which is consistent with the endoergic nature of the proton transfer from *t*-$C_4H_9^+$ to acetonitrile.

If energetically permissible, the role of protonation as a reaction channel competing with alkylation is indirectly supported by the comparatively low yields of alkylation of benzonitrile with *t*-$C_4H_9^+$. In contrast with the analogous transfer to acetonitrile, proton transfer from the tertiary cation to $C_6H_5CN$ is known to be energetically favored.[21] Consequently, process 6 becomes possible and much lower yields of *N*-*tert*-butylbenzamide than that of *N*-*tert*-butylacetamide are obtained. The above evidence for the intervention of proton transfer to nitriles appears however to be in contradiction with the failure to detect acetamide or benzamide among neutral products, which conceivably formed from protonated nitriles according to processes analogous to those described by eq 4 and 5. Even attempts to isolate acetamide as a product from the reaction of $CH_3CN$ with species ($H_3^+$, $H_3O^+$) acting exclusively as strong Brønsted acids were consistently unsuccessful.

This evidence together with the chemical ionization spectra, showing that protonated nitriles are indeed formed as abundant ionic products from the reaction of carbenium ions with nitriles, strongly suggest that the failure to obtain unsubstituted amides must be traced *to the subsequent reactions* of protonated nitriles.

A possible explanation is that protonated nitriles are involved in clustering equilibria with water molecules, which eventually lead to reversible deprotonation, e.g.

$$CH_3CNH^+ + nH_2O \rightleftarrows CH_3CN\cdots{}^+H\cdots(OH_2)_n \rightleftarrows CH_3CN + {}^+H(nH_2O) \qquad (7)$$

rather than in the condensation–deprotonation sequence 4 and 5. In this case, the protonated adducts would behave as effective solvation centers, owing to the high charge density and the clustering ability of the hydrogen atom bound to nitrogen, consistent with the recognized[13] clustering properties of HCN. The lack of a comparably polarized H atom in the alkylated nitriles I explains their tendency to behave rather as Lewis acids toward polar molecules, as illustrated by eq 4.

**Competition of Nitriles with Other Nucleophiles.** Since nitriles are not the only nucleophiles contained in the gaseous system, competition of other reactive species for the carbenium ions can be expected. In the first place, according to eq 4 one must consider water the reagent required to trap nitrilium ion. Water can react with the carbenium ions according to the general addition process

$$R^+ + H_2O \rightarrow ROH_2^+ \qquad (8)$$

which is known[22] to be exothermic for *sec*-$C_3H_7^+$ and *t*-$C_4H_9^+$,

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(19) E.g., $PA(CH_3CONHR) \geq PA(CH_3CONH_2) = 210.4$ kcal $mol^{-1}$, according to Yamdagni and Kebarle (Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1973**, *95*, 3504–3510).

(20) Calculated from the data of Lias et al. (Lias, S. G.; Shold, D. M.; Ausloos, P. *J. Am. Chem. Soc.* **1980**, *102*, 2540–2548).

(21) $\Delta H \simeq -1$ kcal $mol^{-1}$ according to the PA values given by Lau and Kebarle (Lau, Y. K.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 7452–7453).

22.8 and 11.2 kcal $mol^{-1}$, respectively. It is certainly exothermic for *sec*-$C_4H_9^+$. Reaction 8 has been directly demonstrated by radiolytic techniques in gaseous systems at atmospheric pressure.[7] In addition, carbenium ions can protonate water via clustering processes such as

$$C_nH_{2n+1}^+ + nH_2O \rightarrow C_nH_{2n} + H(OH_2)_n^+ \quad (9)$$

whose net result is again to subtract carbenium ions to the reaction with nitriles.

Indeed, the yields of *N*-alkylated amides decrease as the $[H_2O]$:[RCN] ratio is increased. The effect is particularly pronounced in the alkylation of $C_6H_5CN$, whose concentration is limited by its inherently low vapor pressure.

However, water is not particularly suitable for carrying out quantitative competition experiments because of the multiplicity of its reaction pathways and the possibility that ionic products from reaction 8 can alkylate nitriles. This is suggested by the dependence of the tert-butylation yields on the water concentration, whose effect is less pronounced than would be expected by assuming a straightforward competition with the nitrile. Other reference nucleophiles, e.g., $C_6H_6$ and $C_7H_8$, whose alkylation by carbenium ions has been thoroughly investigated in the gas phase,[2] were therefore employed to evaluate the substrate selectivity in the reaction.

**Substrate Selectivity.** The results of the competition experiments show that attack of *t*-$C_4H_9^+$ is biased in favor of the nitriles over arenes and in favor of $CH_3CN$ over $C_6H_5CN$. For secondary carbenium ions, the order is instead $CH_3CN$ > arene > $C_6H_5CN$, with an appreciable discrimination among nitriles. The trend is consistent with the results obtained in the study of ambident nucleophiles, e.g., phenol and anisole, where the attack of the harder tertiary carbon acid is more sharply biased in favor of the *n*-donor center than the attack of the isopropyl cation.[3,4,6]

It must be noted that the apparent $k_{RCN}$:$k_{C_7H_8}$ ratio of >6, which is unusually high for exothermic ion–molecule reactions, represents the *upper limit* of the substrate selectivity.

In fact, it could be affected to some degree by the contribution of the ionic product of reaction 8 whose alkyl group transfer to nitriles, but not to toluene, is energetically allowed.

Competition between $CH_3CN$ and $C_6H_5CN$ for the secondary carbocations could be conceivably affected by the different efficiency of the proton-transfer processes competing with alkylation, arising from the higher PA of the latter substrate. If this were the case, however, one should expect, in contrast with the experimental evidence, an even higher $k_{CH_3CN}$:$k_{C_6H_5CN}$ value for the alkylation by *t*-$C_4H_9^+$ ions, whose conjugate base (*i*-$C_4H_8$) has a PA value intermediate between that of $CH_3CN$ and $C_6H_5CN$.[21]

**Comparison with Solution-Chemistry Studies.** The mechanistic pattern emerging from the present study displays clear analogies with the relevant steps of the addition of alkenes to nitriles in strongly acidic solutions that were originally reported by Ritter.[24] The reaction occurring in solution is believed to involve the formation of an ion pair whose positive partner is a carbenium ion. Attack of the nitrile yields a nitrilium salt, according to a process that represents the solution-chemistry counterpart of reaction 3, followed by hydrolysis to the final product. The Ritter reaction has been extensively investigated, mainly for synthetic purposes, and the scarce kinetic data[25] do not allow meaningful comparison with the gas-phase alkylation. It should be noted, in this connection, that the highly polar solvents used, and the presence of strong acids, entail solvation of the charged center and strong interactions with the counterion. This could well obscure the intrinsic mechanistic behavior of the reagents.

In conclusion, the present study demonstrates, with the degree of confidence allowed by the actual isolation of the key products, the preferred site of alkylation of nitriles by gaseous carbenium ions. This provides unequivocal evidence for the occurrence of nitrilium ions in the dilute gas state. The results allow us to assess the relative reactivity of the *sec*-$C_3H_7^+$, *sec*-$C_4H_9^+$, and *t*-$C_4H_9^+$ cations toward the cyano group and to evaluate the intramolecular and intermolecular selectivity of the attack in the absence of perturbing environmental factors.

The reactivity order for the alkylation of nitriles, i.e., $CH_3CN$ > $C_6H_5CN$, is inverted with respect to the basicity order of the substrates and secondary cations are more selective than *t*-$C_4H_9^+$. The latter reagent sharply discriminates between the nitrogen atom of the cyano group and the $\pi$ electrons of reference aromatic substrates. In no case is aromatic alkylation of $C_6H_5CN$ observed.

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**Registry No.** $CH_3CN$, 75-05-8; $C_6H_5CN$, 100-47-0; $C_2H_5CN$, 107-12-0; *t*-$C_4H_9^+$, 14804-25-2; *sec*-$C_3H_7^+$, 19252-53-0; *sec*-$C_4H_9^+$, 16548-59-7; toluene, 108-88-3.

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[22] Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc.* **1977**, *99*, 360–366 and references cited therein.

[23] According to ref 20, the $\Delta G°$ values (kcal $mol^{-1}$) for the process are: 24.9 (*t*-$C_4H_9^+$), 11.7 (*sec*-$C_3H_7^+$), and 11.6 (*sec*-$C_4H_9^+$).

[24] Ritter, J. J.; Minieri, P. P. *J. Am. Chem. Soc.* **1948**, *70*, 4045–4048.

[25] For a review see: Krimen, L. I.; Cota, D. J. In "Organic Reactions"; Wiley: New York, 1969; Vol. 17, Chapter 3.