For VGSR generation of thioformyl cyanide (**1**) the precursor **7** was vaporized through an external reactor (l = 20 cm, i.d. = 2.5 cm, half-filled with dried K_2CO_3) fitted to the sphere and heated to 220 °C (p = 10^{-2} mbar). The lifetime of **1** in the gas phase (25 °C, 10^{-2} mbar) was obtained by thermolysis of the precursor **2** in an external FVT oven; the observation cell was then isolated by stopcocks from oven and vacuum pumps, and the decay of the absorption recorded.

Acknowledgment. This work was supported in part by the CNRS (GDR PCMI) and by the Région Nord-Pas-de-Calais. The DEMIRM (Observatoire de Paris-Meudon) is gratefully acknowledged for providing us with Shottky barrier diodes.

Supplementary Material Available: Millimeter wave spectrum of thioformyl cyanide in the ground vibrational state between 130 and 280 GHz (measured and calculated frequencies) (3 pages). Ordering information is given on any current masthead page.

Vinylation of Aromatic Substrates by Free Unsolvated Vinyl Cation in the Gaseous and Liquid Phase

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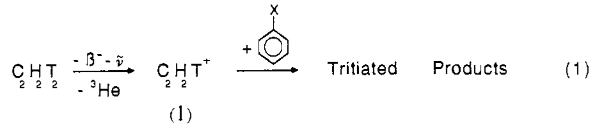
Abstract: The nuclear-decay technique has been employed to generate free, unsolvated vinyl cation, $C_2H_2T^+$, and to investigate its reactivity and selectivity toward substituted arenes both in the gas phase and in the liquid phase. The differences between the reactivity pattern of unsubstituted vinyl cation in the two environments are rationalized in terms of the much greater efficiency of collisional stabilization in the condensed phase, allowing a larger fraction of the excited arenium ions, from the highly exothermic ($-\Delta H° > 73$ kcal mol^{-1}) attack of the vinyl cation on the selected aromatics, to survive dissociation. An additional difference arises from a change of the nature of the vinylating reactant, when additives, such as Ar or CO, are introduced into the gaseous mixtures. The mechanisms of the two major competitive processes promoted by $C_2H_2T^+$ attack on substituted arenes, i.e. vinylation and tritonation, as well as the isomerization pathways of the ensuing adducts as a function of the experimental conditions, are discussed and compared with related results. The present study allows the first experimental evaluation of the substrate and positional selectivity of a very elusive species, such as $C_2H_3^+$, which is compared with that of other reactive gaseous electrophiles and of more conventional vinylating reagents produced under solvolytic conditions.

Substituted vinyl cations are now recognized organic intermediates,[1] some of them stable enough to be directly observable by ^1H and ^{13}C NMR spectroscopy under non-nucleophilic conditions.[2] However, very little is known as to the actual occurrence and the reactivity of the unsubstituted vinyl cation. In fact, generation of $C_2H_3^+$ in solution is an interesting challenge that was first undertaken by Berthelot as long ago as 1862.[3] His studies, and those of others over the following 20 years, established that acetylene is converted, in H_2SO_4, first into acetaldehyde and then into crotonaldehyde. More recently, Olah et al.[4] showed that the reaction of acetylene with FSO_3H at low temperatures gives vinyl fluorosulfate, which, however, decomposed above −15 °C. Then, Tidwell et al.[5] carried out a quantitative study of the reactions taking place in C_2H_2/90–95% H_2SO_4 mixtures at 25 °C in an attempt to determine spectroscopically whether $C_2H_3^+$ is involved.

In the gas phase, $C_2H_3^+$ ions can easily be produced by mass spectrometry and their heat of formation evaluated.[6] A number of mass spectrometric investigations have been carried out to determine the reactivity pattern of $C_2H_3^+$ ions with simple hydrocarbons and to measure the rate constants for the formation of the charged products.[7] In these approaches, a major difficulty is found in the largely variable energy content of the encounter complex between the vinyl cation and the substrate molecule, which makes kinetic measurements[8] and product distribution[9] appreciably dependent upon the method adopted and, in any event, hardly comparable with those from the same processes occurring between thermally equilibrated species in the condensed phase.

This difficulty has been recently overcome by resorting to the nuclear-decay technique,[10] which allowed us to obtain electronically ground-state vinyl cations by spontaneous β-decay in bitritiated ethylene in both gaseous and liquid phase (eq 1).[11] By



$$C_2H_2T_2 \xrightarrow[-\,^3He]{-\beta^-\,-\,\bar{\nu}} C_2H_2T^+ \xrightarrow{+C_6H_5X} \text{Tritiated Products} \qquad (1)$$

X = H, Me, F, Cl, Br, OMe

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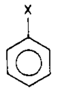
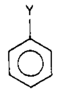
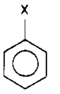
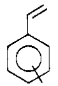
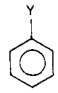
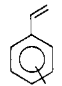
Table I. Tritiated Products from the Attack of Tritiated Vinyl Ions on Gaseous Arenes

syst composition[a] (Torr)			relative yields of products,[b] %									
		other additives (Torr)					other products	total absolute yield,[c] %	composition of substituted styrenes, % ortho	meta	para	apparent[d] $k_{C_6H_5X}/k_{C_6H_5Y}$
X = Me (16.4)	Y = H (2.8)		59.8	18.9	16.3	4.9		31.8	14	68	18	0.7
X = Me (11.0)	Y = H (9.6)		37.9	14.0	36.5	11.6		22.6	23	65	12	1.1
X = Me (10.2)	Y = H (10.8)	He (720)	35.6	19.1	30.6	14.7		18.9	14	71	15	1.4
X = Me (10.6)	Y = H (10.8)	Ar (720)	13.9	41.0	15.2	29.9		74.7	17	69	14	1.4
	Y = H (6.3)	CO (180)			59.2	40.8		9.8				
X = Me (4.7)		CO (720)	84.0	16.0				7.5	8	66	26	
X = Me (5.1)		CO (180)	74.5	25.5				8.2	13	66	21	
X = Me (6.0)		CO (45)	64.0	36.0				21.4	14	70	16	
X = F (18.0)	Y = H (2.7)		61.9	24.9	9.9	3.2		22.8	21	69	10	1.2
X = F (10.0)	Y = H (10.3)		33.9	19.8	31.9	14.3		27.8	19	76	5	1.4
X = F (10.2)	Y = H (10.4)	Ar (720)	31.2	24.9	29.9	14.0		59.1	20	75	5	1.8
X = Cl (12.0)			97.3	2.4			0.1;[e] 0.2[f]	32.1	22	68	10	
X = Cl (6.1)	Y = H (15.0)		20.3	4.3	58.0	17.4		32.2	19	64	16	0.6
X = Br (1.8)			60.6	nd[g]			39.4[h]	6.6				
X = Br (1.9)	Y = H (10.1)		5.5	nd[g]	75.7	14.9	3.9[h]	17.4				1.4
Y = OMe (2.0)			71.2	16.9			8.8;[i] 3.1[j]	17.1	8	80	12	
Y = OMe (2.1)	Y = H (9.6)		21.6	6.6	51.8	17.1	2.4;[i] 0.5[j]	24.6	6	67	27	2.6
Y = OMe (2.0)	Y = H (11.2)	Ar (720)	13.8	20.7	44.8	14.9	2.7;[i] 3.1[j]	48.0	12	60	28	9.6

[a] All gaseous systems contain O_2 (4 Torr), NMe_3 (0.3 Torr), and tritiated ethylene (ca. 1–2 mCi). [b] Ratio of the activity of each product to the combined activity of all products identified. [c] Ratio of the total activity of the identified products to the activity originally contained in the nuclear-decay formed vinyl cation. Each value is the average of several determinations, with an uncertainty level of ca. 10%. [d] Apparent values, not corrected (see text). [e] Styrene. [f] Phenylacetylene. [g] Nd: below detection limit, 0.5% absolute yield. [h] Vinyl bromide. [i] Phenyl vinyl ether. [j] Allyl phenyl ether.

this method, a first insight into the reactivity of tritiated vinyl cation (I) toward simple molecules, such as H_2,[8b] CH_4,[8b] CH_3OH,[11] and benzene,[9b,11] was directly obtained, based on the comparative analysis of kinetic data and product distribution under largely different conditions, ranging from relatively low pressure (6 Torr) gases to liquids.

In the present study, we focus attention on the reactivity and selectivity features of the vinyl cation (I) from nuclear decay toward substituted arenes both in the gas phase at different pressures and in the liquid phase (eq 1). The choice of the reaction was suggested in the first place by the potential value of this very simple aromatic substitution as a model for electrophilic vinylation reactions in solution, where the unstable and extremely reactive vinyl cation $C_2H_3^+$ cannot be conveniently obtained in the free state, in contrast with the more stable substituted vinyl cations. Furthermore, substituted arenes appear suitable substrates for extending our knowledge to the otherwise largely unexplored area concerning the reactivity properties of the parent $C_2H_3^+$ cation. Finally, the nuclear origin of the $C_2H_3^+$ cation discloses the intriguing possibility of investigating the reactivity pattern of the $C_2H_3^+$ ion–aromatic compound pair exclusively as a function of the variables that define the reaction environment.

Experimental Section

Materials. The preparation and the purification of ethylene, containing at least two tritium atoms in the same molecule, used as a source of the decay vinyl cation, have been described elsewhere.[11] He, Ar, O_2, NMe_3, and CO were obtained from Matheson Gas Products, Inc., their stated purity exceeding 99.3 mol %. Aldrich Chemical Co. and Fluka AG provided all the other products used as reference compounds or as reactants in the nuclear-decay experiments. *o*- and *m*-Methoxystyrene,[12] *o*-fluorostyrene,[13] phenyl vinyl ether,[14] α- and β-methyldihydrobenzofuran,[12,15] and isomeric phenyl propenyl ethers[14,16] were prepared according to established procedures.

Decay Experiments. The gaseous samples were prepared by conventional vacuum techniques, introducing tritiated ethylene (ca. 1–2 mCi), diluted with inactive ethylene to a specific activity of 363 Ci mol^{-1}, into evacuated and carefully outgassed 250-mL Pyrex vessels containing a measured amount of the aromatic substrate(s) together with appropriate additives (He, Ar, CO, O_2, and NMe_3). The vessels were then sealed off and stored for 10–14 months in the dark at room temperature. The composition of the gaseous decay systems is given in Table I.

The liquid samples were prepared according to the following procedure: ca. 1–2 mCi of the bitritiated ethylene mixture (specific activity 363 Ci mol^{-1}) were introduced into carefully evacuated and outgassed Pyrex vials (5 mL), equipped with a long capillary arm closed by a fragile tip. Each vial was sealed off from the vacuum line, and its capillary arm was introduced into a cylindrical vessel containing at the bottom a layer of purified mercury and ca. 7 mL of the aromatic substrate(s), which had been previously outgassed and washed with O_2. The fragile tip of the capillary arm was then broken under the level of the aromatic mixture, which was consequently forced into the evacuated vial. When only a small bubble of gas was left at the top of the vial, the capillary arm was lowered further into the mercury. After a few hours, the vial was entirely filled by the aromatic mixture, except for the lower portion of the capillary, where the mercury has risen, acting as a mobile seal. The vials were stored in the dark, at room temperature, for ca. 10–14 months. The composition of the liquid decay systems is shown in Table II.

After the storage period, the sealed ampules were opened under airtight conditions and their contents analyzed on a C. Erba Fractovap 4200 gas chromatograph equipped with a high-sensitivity hot-wire detector (Model 450) coupled in series with a Berthold proportional flow counter kept at 180 °C. Small portions of the homogeneous decay mixtures were withdrawn with a syringe and injected directly in order to analyze their tritiated components. In some cases, the reaction vessels containing the gaseous decay mixtures were cooled and thoroughly washed with ethyl acetate. Measured aliquots of the acetate solutions were injected into the radio gas chromatograph.

The tritiated products were identified by comparing their retention volumes with those of authentic samples on the following columns: (a) a 2-m-long stainless steel column containing 5% SP 1200:5% Bentone 34 on 100–120 mesh Supelcoport, operated at temperatures ranging from 100 to 120 °C; (b) a 2-m-long glass column containing 1% SP 1000 on Carbopack B, operated at temperatures ranging from 30 to 190 °C; (c) a 6-m-long stainless steel column containing 20% E 301 on 60–80 mesh Chromosorb W, operated at temperatures ranging from 100 to 150 °C.

Results

The relative yields of the tritiated products from the attack of the nuclear-decay formed vinyl cations on the selected substituted arenes, and the isomeric composition of the substituted styrenes formed, are given in Table I for the gaseous systems and in Table II for the liquid ones.

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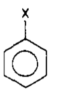
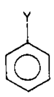
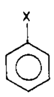
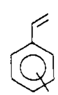
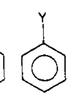
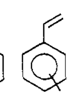
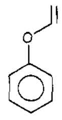
Table II. Tritiated Products from the Attack of Tritiated Vinyl Ions on Liquid Arenes

system composition,[a] mol %		relative yields of products,[b] %									
							total absolute yield,[c] %	composition of substituted styrenes, %			apparent[d] $k_{C_6H_5X}$ / $k_{C_6H_5Y}$
								ortho	meta	para	
X = Me (100)		21.9	78.1				52.0	39	30	31	
X = Me (75)	Y = H (25)	20.9	56.5	5.6	17.0		45.6	44	30	26	1.1
X = Cl (100)		19.5	80.5				57.5	57	24	19	
X = Cl (25)	Y = H (75)	2.8	11.1	43.0	43.1		31.2	48	26	26	0.8
X = Cl (50)	Y = Me (50)	4.3	17.4	55.9	22.4		20.8	35 (X); 38 (Y)	37 (X); 38 (Y)	27 (X); 24 (Y)	0.8
X = Br (75)	Y = H (25)	10.1	40.5	29.6	19.8		32.9	44	32	23	0.7
X = OMe (100)		42.5	53.8			3.7	30.8	56	18	26	
X = OMe (75)	Y = H (25)	12.7	48.8	19.0	11.2	8.3	46.0	43	28	29	1.7
X = OMe (25)	Y = H (75)	3.8	21.3	38.9	31.3	4.5	29.7	40	30	30	2.5
X = OMe (50)	Y = Me (50)	8.0	42.0	30.2	16.4	3.4	36.6	40 (X); 51 (Y)	31 (X); 26 (Y)	29 (X); 23 (Y)	2.6
X = OMe (50)	Y = Cl (50)	19.2	44.6	11.2	17.9	7.1	42.8	45 (X); 55 (Y)	26 (X); 20 (Y)	29 (X); 25 (Y)	2.5

[a] All liquid systems are saturated with O_2 and contain tritiated ethylene (ca. 1–2 mCi). [b] See footnote *b* of Table I. [c] See footnote *c* of Table I. [d] See footnote *d* of Table I.

The absolute yields, defined by the ratio of the activity of the products to the total activity of the vinyl cations formed within the system can be calculated from the initial activity and the isotopic composition of tritiated ethylene, the decay rate of tritium, the abundance of the vinyl cations among the decay fragments taken as ca. 80%,[17] and the absolute counting efficiency of the detector employed. These admittedly crude calculations show that the products identified account for ca. 19–75% of the activity contained in the decay ions, without significant differences among the various gaseous and liquid systems investigated. Appreciably lower absolute yields of tritiated products are instead measured in the gaseous decay systems containing bromobenzene as substrate (6.6–17.4%) or carbon monoxide as additive (7.5–21.4%). Furthermore, the total activity of the crude tritiated arenes, after removal of undecayed tritiated ethylene and other low-boiling products, has been found to match almost exactly the combined activity of the products identified by radio GLC, excluding the presence of other significant labeled products (e.g. dimers, oligomers, polymers, etc.) in the decay samples and suggesting that the activity balance must instead be provided by some gaseous species, most likely HT, tritiated acetylene, or tritiated ethylene, arising either directly from fragmentation processes or deriving from the direct attack of vinyl cation to the substrates or additives present.

Analysis of Table I reveals that the tritiated substrate(s) and the corresponding substituted styrenes are invariably the major labeled products, accompanied by minor amounts of vinyl bromide (X = Br), phenyl vinyl ether and allyl phenyl ether (X = OMe), styrene, and phenylacetylene (X = Cl). Their absolute yield and relative distribution in the gaseous samples appear greatly affected by the presence and the nature of the additive. In particular, while addition of 720 Torr of He does not cause any significant change in the product distribution, a dramatic increase of the relative and absolute yield of the styrene products is generally observed, as 720 Torr of Ar are added to the gaseous mixture. When, instead, CO is used as additive, a significant decrease of the overall absolute product yield is observed, arising from a decrease of both the tritiated substrate and the styrene yields. It should be noted that the effect is more pronounced at high CO partial pressures (720 Torr). The effect of the additives is extended as well as regards to the apparent relative substrate reactivity, expressed by the $k(C_6H_5X)/k(C_6H_5Y)$ ratios. The relevant figures, evaluated by assuming a first-order dependence of the vinylation rates on the substrates concentration, appear to increase in the presence of 720 Torr of Ar (Table I).

The isomeric composition of the vinylated products from all selected substrates indicates the predominant formation of the meta isomer (60–80%) under all conditions, with no or very limited (X = OMe) influence of the gaseous additives. When X = Br, the only observed vinylation product is vinyl bromide, from attack of $C_2H_3^+$ at the Br atom of the aromatic substrate. A corresponding product, namely phenyl vinyl ether, accompanies formation of isomeric methoxystyrenes from anisole (X = OMe). Apart from allyl phenyl ether, no other labeled products, such as α- and β-methyldihydrobenzofuran, α- and β-methylbenzofuran, 3,4-dihydro-2*H*-1-benzopyran, isomeric phenyl propenyl ethers, isomeric β-methoxystyrenes, phenylacetaldehyde, and acetophenone, are recovered from the decay samples containing anisole.

A qualitatively similar product pattern arises from the decay samples containing the selected arenes in the liquid state (Table II). Here, however, the relative yields of the styrene products are comparatively much higher than those of the tritiated substrate(s), including X = Br. In analogy with the relevant gaseous samples, minor amounts of phenyl vinyl ether accompany formation of isomeric methoxy styrenes in the decay runs with liquid anisole. On the contrary, no measurable amounts of vinyl bromide have been recovered among the tritiated products from liquid bromobenzene, which contrasts with the significant yields of the same product from the corresponding gaseous systems. The isomeric composition of products from attack of $C_2H_3^+$ on liquid substituted arenes is substantially different from that observed in the gaseous samples, being characterized by the predominant ortho and para isomers orientation.

Discussion

Nature of the Ionic Reactant. The formation of tritiated vinyl cation from the decay of tritiated ethylene has been discussed in detail elsewhere (eq 1).[8b,9b,11] The vinyl cation, formed in its electronic ground state, is characterized by excess internal energy due, inter alia, to the relaxation from its original geometry, reminiscent of the parent ethylene, to that of the most stable structure, which, according to very refined ab initio calculations, can be either the nonclassical proton-bridged π-protonated acetylene or the classical acyclic vinyl cation.[18] In the extreme hypothesis of an overall adiabatic process for the formation of vinyl cation from the nuclear transition, semiempirical calculations set an upper limit of ca. 50 kcal mol^{-1} to its vibrational excitation.[19] Such an excess of internal energy in the nuclear-decay formed vinyl cation may affect its reactivity and selectivity properties toward the selected substrates. Accordingly, significant changes in the apparent substrate and positional selectivity of the $C_2H_3^+$ ion are observed when the gas-phase experiments are carried out in the presence of appropriate additives, such as Ar or CO, which favor collisional quenching of the vinylating reactant and, in some instances, may

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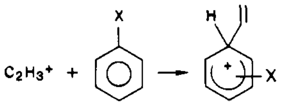
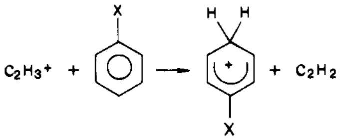
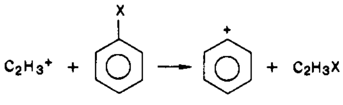
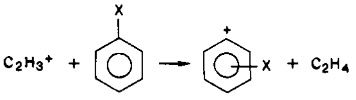
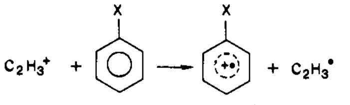
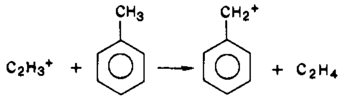
(19) (a) Sustmann, R.; Williams, J. E., Jr.; Dewar, J. M. S.; Allen, L. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1969**, *91*, 5350. (b) Hopkins, A. C.; Yates, K.; Csizmadia, I. G. *J. Chem. Phys.* **1971**, *55*, 3835.

(20) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

Table III. Energetics of Several Relevant Reactions of Vinyl Cation with Substituted Benzenes[a]

process	$\Delta H°$ for given X's, kcal mol^{-1}					
	H	Cl	Br	F	Me	OMe
(i) 	≤-73[b]	≤-73[b]	≤-73[b]	≤-73[b]	≤-73[b]	≤-73[b]
(ii) 	-28	-28	-29	-29	-36	-47
(iii) 	-4	0	-2	-1	-33	-4
(iv) 	-4	≅-4[c]	≅-4[c]	≅-4[c]	≅-4[c]	≅-4[c]
(v) 	+7	+11	+10	+14	-3	-9
(vi) 					-55	

[a] The formation enthalpies of the ions and the neutrals used for these calculations have been taken from ref 20. Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969. Vedeneyev, V. I.; Gurvich, L. V.; Kondrat'yev, Y. N.; Medvedev, V. A.; Fankevich, Ye. L. *Bond Energies, Ionization Potentials and Electron Affinities*; Edward Arnold Publ., Ltd.: London, 1966. [b] Only the upper limit of these reaction enthalpies can be estimated by assuming a stabilizing substituent effect in the primary ionic adduct and the proton affinity at the ring position bearing the vinyl groups of the relevant styrene as equal to that of the same position in the corresponding arene. [c] Only an approximate value of these reaction enthalpies can be estimated by assuming a negligible substituent effect in the primary arylium ions, $\Delta H_f°$ ($C_6H_5^+$) taken as equal to 271 kcal mol^{-1}.[20]

modify its nature prior to attack on the arene. Collisional deactivation may prevent isomerization and fragmentation of the primary vinylation adducts as well. This effect is expected to be particularly important in the liquid phase, owing to the exceedingly high collision frequency (ca. 10^{13} s^{-1}).

Several exothermic reaction channels are available to the vinyl cation in its attack on the aromatic substrates, as illustrated in Table III, providing approximate $\Delta H°$ values for several relevant processes, calculated from the $\Delta H°_f$ value of vibrationally ground-state gaseous $C_2H_3^+$ (267 kcal mol^{-1}),[6a,b] which is appropriate for the gaseous systems and represents a rough approximation for the liquid-phase reactions, even considering the low degree of solvation of the electrophile.[21] If allowance is made for the excess vibrational energy of the decay-formed $C_2H_3^+$ that could enhance the enthalpy changes of the processes of Table III by up to 50 kcal mol^{-1}, occurrence of the slightly endothermic but entropically favored charge exchange reaction v cannot be, in principle, excluded. Thus, while exothermic reactions i–iii of Table III may be considered as the most likely sources of the radioactive products recovered from the decay experiments, several other "blind" channels (i.e. not leading to labeled products other than the starting ethylene), namely the thermodynamically allowed reactions iv–vi, may be operative, which could account for the activity loss measured in the decay samples. However, reaction v would lead to the inactive arene molecular ion and to the tritiated vinyl radical, whose contribution, if any, to the identified products should be negligible, in view of the appreciable increase of the absolute yields of products from both gaseous and liquid toluene observed at increasing concentrations of the aromatic substrate (Tables I and II). In fact, toluene is known[22] to react with alkyl radicals by efficient side-chain hydrogen abstraction yielding the benzyl radical. As a consequence, if pathway v were significant, labeled product yields from the systems containing toluene are expected to be unaffected or even to undergo a significant decrease by increasing the toluene concentration, at variance with the experimental evidence. The same evidence excludes as well a significant role of the highly exothermic hydride ion transfer vi. On the contrary, the hydride ion abstraction iv may well occur in the decay samples yielding tritiated ethylene, which cannot be discriminated from the starting tritiated ethylene, together with unlabeled products from the substituted phenyl cation fragment.

Liquid-Phase Reactions. In the discussion of vinyl cation attack on the selected arenes, it is convenient to consider first the liquid-phase reaction, whose features fit into the familiary picture of conventional solution-chemistry reactions, displaying, in particular, considerable similarity with aromatic substitution by highly reactive and poorly solvated alkylating electrophiles.[23]

The evidence reported in Table II is, in fact, consistent with a straightforward reaction sequence, initiated by the highly exothermic attack of the vinyl cation to the π-system of the aromatic substrate, yielding excited arenium ions (eq i), whose fragmentation and/or isomerization, very extensive in the dilute gas state (vide infra), undergo effective competition by the fast collisional deactivation typical of the liquid environment.[11] Deprotonation of the stabilized arenium ions by any base contained in the system, including NMe_3 or the substrate itself, provides a direct route to the substituted styrenes. Formation of minor yields of phenyl vinyl ether (3.4–8.3%), accompanying meth-

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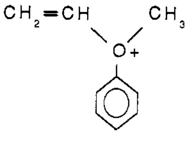
(21) The nuclear process leading to vinyl cation is fast relative to bond vibration (ca. 10^{-14} s). As a consequence, formation of vinyl cation is entirely insensitive to environmental factors, being equally effective in the gaseous and condensed phase. In this respect, the decay ion is formed as unsolvated species in the gas phase. In the liquid phase, it is formed in the same solvation state as its ethylene precursor and its reaction with the substrate occurs well before an organized solvation shell had time to assemble. In addition, the decay-formed ionic reactant is not associated to any counterion, its positive change being balanced by the far-removed β^- particle.

(22) (a) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465. (b) Szwarc, M. *Ibid.* **1950**, *47*, 75.

(23) (a) Cacace, F.; Giacomello, P. *J. Chem. Soc., Perkin Trans. 2* **1978**, 652. (b) Giacomello, P. *J. Am. Chem. Soc.* **1979**, *101*, 4276.

oxystyrenes from anisole, indicates partial attack of the vinyl cation to the n-type center of the substrate, yielding the intermediate onium ion (II).



(II)

In principle, ion II, excited by the exothermicity of the attack, could either decompose unimolecularly to phenyl vinyl ether ($+CH_3^+$; $\Delta H°$ ca. +15 kcal mol^{-1}) or, alternatively, to methyl vinyl ether ($+C_6H_5^+$; eq iii; $\Delta H°$ ca. -4 kcal mol^{-1}). Especially in the liquid phase, it could as well undergo collisional stabilization and, eventually, nucleophilic attack by another molecule of the substrate, present in large excess. In this latter case, predominant formation of labeled phenyl vinyl ether is expected, owing to the higher propensity of the C_{sp^3} atom of the methyl group to undergo nucleophilic attack when compared to the α-C_{sp^2} centers of the phenyl and of the vinyl moieties of II. The exclusive formation of phenyl vinyl ether among the labeled products from anisole (Table II) points to the occurrence of a bimolecular nucleophilic attack at the methyl group of II, ruling out any significant unimolecular fragmentation of excited II, which would rather produce preferentially labeled methyl vinyl ether ($+C_6H_5^+$, reaction iii, Table III) on account of its more favorable energy requirements. It is concluded that anisole behaves as a bidentate nucleophile,[24] which undergoes attack by $C_2H_3^+$ on both its π-system and n-type center, yielding, in the latter case, an onium intermediate II, which is stabilized in the liquid phase and is able to undergo further attack at the methyl group by the nucleophiles present in the liquid mixture. A similar process may, in principle, take place as well in all other selected substrates, containing an n-type center, i.e., halobenzenes. Here, however, stabilized phenyl vinyl halonium ions would be formed, where further nucleophilic attack by another substrate molecule is bound to occur at one of the two C_{sp^2} centers α to the halogen atom. The lack of measurable amounts of labeled vinyl halides from these systems spells in favor of a more effective attack on the vinylic α-C_{sp^2} center rather than on the aromatic one.

Recovery of minor but significant amounts of tritiated substrates from the liquid decay systems of Table II can be traced to partial fragmentation of the corresponding excited arenium ions from eq i, although occurrence of the direct triton transfer ii (Table III) cannot be a priori excluded. In both cases, labeled acetylene is expected to be formed as byproduct and actually observed among the volatile products, in absolute yield approaching twice as much as that of the corresponding tritiated substrate.

The conceivable occurrence of residual fragmentation and, perhaps, isomerization of the excited arenium ions from eq i, even in the liquid phase, undoubtedly complicates the evaluation of the substrate and positional selectivity of the vinyl cation. However, restricting the comparison to the vinylation channel, the results of Table II point to the rather unselective character of the vinyl cation, barely capable of discriminating among the aromatic substrates chosen. The positional selectivity deduced from the isomeric composition of the substituted styrenes must be regarded as a lower limit, owing to the possible isomerization of a fraction of the initially formed ortho and para vinylated intermediates to the meta one, that is thermodynamically the most stable, as discussed in the next section. Despite this possibility, a limited, yet well-measurable preference of the vinyl cation for ortho–para attack is apparent from the isomeric composition of the substituted styrenes of Table II, reflected by para:$^1/_2$meta ratios ranging from ca. 1.7 (X = Me), ca. 1.9 (X = Cl), ca. 1.4 (X = Br), to ca. 2.2 (X = OMe). Finally, analysis of the corresponding para:$^1/_2$ortho ratios (ca. 1.2 (X = Me); ca. 1.0 (X = Cl, Br); ca. 1.3 (X = OMe)) reveals a slight preference of the vinyl cation for the para position of toluene and anisole, without appreciable discrimination between ortho and para positions of chloro- and bromobenzene.

Gas-Phase Reactions. In contrast with the efficiency of collisional deactivation in the liquid, the gas-phase picture is dominated by extensive isomerization and fragmentation processes affecting the excited arenium ions from reaction i (Table III). Such a trend is well documented by the predominant formation of the tritiated substrates among the reaction products (Table I), traced essentially to a more extensive fragmentation of the primary, excited vinylated adducts, including onium intermediates (e.g. II), when formed. Furthermore, the composition of the substituted styrenes formed is invariably shifted in favor of the meta isomer, which becomes by far the most abundant (65–71% (X = Me; 69–76% (X = F); 64–68% (X = Cl); 60–80% (X = OMe))(Table I).

Such interpretation is in part demonstrated by the effects of the additives on the products pattern. Thus, when the collision frequency of the ionic species with the bath gas is increased by several orders of magnitude, e.g. by adding 720 Torr of He or Ar to the mixture, a significant decrease of the yield of the tritiated starting substrate(s) is observed, which is paralleled by an increase of that of the vinylation products.

However, comparative analysis of the toluene runs with He, Ar, or CO as additives (Table I) suggests that the corresponding changes in the product pattern cannot be related only to the quenching efficiency of the additive, but some other more specific effect, related to the actual nature of the vinylating reactant, may be operative. In fact, addition of 720 Torr of He causes only a slight decrease of the absolute yield of the tritiated substrate(s) (from 16.8 to 12.5%), which is entirely attributable to the increased collisional quenching of the relevant excited vinylation intermediates (eq i). However, replacement of He with Ar induces a dramatic increase of the styrene products yield (from 5.8 to ca. 53% (X = Me); from 9.5 to ca. 23% (X = F); from 5.8 to ca. 17% (X = OMe)), which can hardly be explained exclusively by the different quenching efficiency of the two noble gases. Here, it is tempting to invoke a milder vinylating reactant, formed by combination of Ar with the exceedingly reactive $C_2H_3^+$ ion, i.e. $C_2H_3Ar^+$,[25] as the major responsible of the less extensive fragmentation of the ensuing vinylation adducts and the appreciable changes in the apparent $k(C_6H_5X)/k(C_6H_5Y)$ ratios (Table I), which increase by somewhat 30% (X = Me, F; Y = H) and 250% (X = OMe; Y = H), in the presence of the additive.

The change of products pattern is even more dramatic when CO is added to the gaseous mixture. Here, a pronounced decrease of the absolute yields of both the tritiated substrate (e.g. from 16.8 to 6.3%, with 720 Torr of CO) and of the styrene products (e.g. from 5.8 to 1.2%, with 720 Torr of CO) occurs. This behavior is consistent with the addition of the decay-formed vinyl cation to the carbon monoxide, yielding either $C_2H_3O^+{=}C$ or $C_2H_3C^+{=}O$ isomers,[26] in competition with direct $C_2H_3^+$ attack on the aromatic substrate. In analogy with the conclusions of previous related studies,[26] the relative distributions of the two isomeric $C_3H_3O^+$ structures as well as their back-dissociation to the reactants are expected to depend essentially on the total pressure of the system. Accordingly, the products pattern from the CO runs changes appreciably with the CO partial pressure, the total absolute yield of the styrene products increasing at low CO pressures, namely under conditions favoring back-dissociation of $C_3H_3O^+$ to stabilized $C_2H_3^+$ and CO.

The profound effects of the additives are not displayed in the isomeric composition of the substituted styrenes from aromatic vinylation, which appears essentially independent on the presence and the nature of the additives (Table I). This observation points

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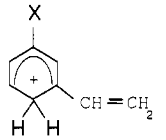
[24] (a) Attinà, M.; Cacace, F.; Ciranni, G.; Giacomello, P. *J. Chem. Soc., Chem. Commun.* **1976**, 466. (b) Attinà, M.; Cacace, F.; Ciranni, G.; Giacomello, P. *J. Am. Chem. Soc.* **1977**, *99*, 4101. (c) Attinà, M.; Cacace, F.; Ciranni, G.; Giacomello, P. *J. Chem. Soc., Perkin Trans. 2* **1979**, 891. (d) Pepe, N.; Speranza, M. *Ibid.* **1981**, 1430.

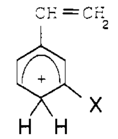
[25] (a) Ausloos, P.; Lias, S. G. *Discuss. Faraday Soc.* **1965**, *39*, 36. (b) Cacace, F., Cipollini, R.; Ciranni, G. *Radiochem. Radioanal. Lett.* **1970**, *4*, 51.

[26] Occhiucci, G.; Cacace, F.; Speranza, M. *J. Am. Chem. Soc.* **1986**, *108*, 872, and references cited herein.

to rapid vinyl group migration within the arenium ions from eq i, irrespective of their excitation energy, leading to the thermodynamically most stable arenium ion structure, which, according to the substituted styrene distribution of Table I, appears to be either III and/or IV.

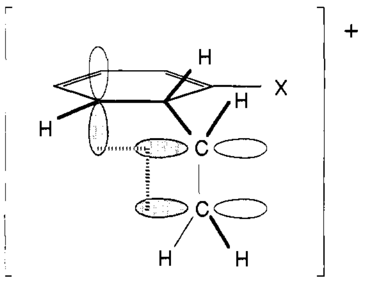


(III)



(IV)

Such a pronounced migrating ability is typical of unsaturated groups,[27] where the transition state for a concerted 1,2-shift may be stabilized by bonding interactions of the migrating substituent with the adjacent reaction center, as shown in V. The same



(V)

stereoelectronic configuration of structure V helps in explaining the predominance of 1,2 vinyl group shift over the competing hydrogen transfer from the ring ipso position of V to the unsaturated side chain to give eventually the thermodynamically most stable α-methyl benzylic structure,[9b] a process that would immediately suppress vinyl group transfer within V.

Conclusions. The present investigation of the reactivity and selectivity properties of unsubstituted vinyl cation, $C_2H_3^+$, is allowed by the unique features of the nuclear-decay technique, which permits generation of free cationic electrophiles of defined structure and energy content from multitritiated hydrocarbon precursors, namely ethylene in the present study. The unparalleled constancy of the nature of the nuclear-decay formed vinyl cation over an extended range of physical conditions affords the unusual possibility of evaluating the reactivity pattern of an otherwise elusive electrophile in largely different media, as a function of the reaction environment. A rationale for the observed differences in reactivity of $C_2H_3^+$ toward the selected aromatic substrates in liquid and gaseous systems can be found in the greatly enhanced efficiency of collisional stabilization in the liquid media, which allows a much larger fraction of the excited arenium ions from reaction i to survive fragmentation and isomerization. An additional reason for the different reactivity can arise from a change in the actual nature of the vinylating reactant in the gaseous systems, when additives, such as Ar or CO, are present.

To our knowledge, in the search to substantiate the long-postulated[4,5] occurrence of the unsubstituted vinyl cation $C_2H_3^+$ in non-nucleophilic solvents, the present study provides the first data concerning the reactivity of an unsolvated $C_2H_3^+$ cation, free of any counterions[21] even in the liquid phase. Consequently, a comparison of the $C_2H_3^+$ reactivity with that of a few typical representatives of more tractable trisubstituted vinyl cations in solution appears of interest.

Significantly, the substrate and positional selectivity of the free $C_2H_3^+$ cation, while extremely close to that of other very reactive, unsolvated cations, such as CH_3^+,[23] is largely different from those of more stable but heavily encumbered trisubstituted vinyl cations, such as those arising from the solvolysis of 1-anisyl-2,2-diphenylvinyl bromide[28] and of 1-phenyl-2,2-dimethylvinyl triflate.[29] In fact, the vinylating reactants formed from these precursors display a substrate selectivity spanning over at least 3 orders of magnitude from chlorobenzene to anisole, whereas their positional selectivity, although characterized by the expected ortho–para distribution, shows a very pronounced preference for the less encumbered para position ($4.6 < \text{para}:{}^1/_2\text{ortho} < 78$).

Acknowledgment. This work was supported by grants from the Ministero della Pubblica Istruzione and from the Strategic Project "Dinamica Molecolare e Catalisi" of the Consiglio Nazionale delle Ricerche of Italy.

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(27) Bach, R. D.; Lucast, D. H. *J. Chem. Soc., Chem. Commun.* **1979**, 593.

(28) Kitamura, T.; Kobayashi, S.; Taniguchi, H.; Rappoport, Z. *J. Org. Chem.* **1982**, *47*, 5003.

(29) Stang, P. J.; Anderson, A. G. *J. Am. Chem. Soc.* **1978**, *100*, 1520.

Photoluminescence of Cubic Mixed-Metal Tetrameric Clusters

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Abstract: The low-temperature luminescence spectra of tetrameric mixed-metal clusters of the type $(DENC)_3Cu_3M(NS)Cl_4$ and $(DENC)_3Cu^I{}_2Cu^{II}Co(NS)_2Cl_4$ (DENC = *N,N*-diethylnicotinamide; NS^- = *S*-methylhydrazinecarbodithioate Schiff base; and M = Co(II), Ni(II), Cu(II), or Zn(II)) in anhydrous methylene chloride are reported. The parent cluster containing four Cu(I) atoms emits at 15 100 cm^{-1}. The clusters containing three Cu(I) atoms and a fourth first-row transition metal emit at λ_{max} = 13 500 cm^{-1} for M = Co(II), λ_{max} = 14 000 cm^{-1} for M = Ni(II), λ_{max} = 13 150 cm^{-1} for M = Cu(II), and λ_{max} = 15 000 cm^{-1} for M = Zn(II). The cluster containing two Cu^I, one Cu^{II}, and one Co^{II} emits at 13 300 cm^{-1}. The emission from all of the clusters is centered on the coppers (not on the ligands or the other metals) and is related to the $3d^94s^1$ excited state strongly modified by copper–copper interactions. The presence of the other metals only slightly perturbs the energy of the emission centered on the coppers. In the case of the mixed-metal clusters containing Co(II) and Cu(II) metals in the core, the emission is not from the lowest excited state of the cluster. In these cases ligand field states centered on the M(II) are lower in energy than the Cu(I) centered emitting state. The emission lifetimes are shortest for the clusters with low-lying d–d excited states.

The luminescence of tetrameric copper cluster compounds is attracting increasing interest.[1–7] These clusters contain the cubic core consisting of four copper(I) ions and four halide ions shown below. Generally, nitrogen-donor ligands such as pyridine and

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