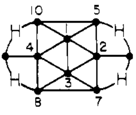
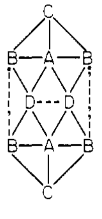
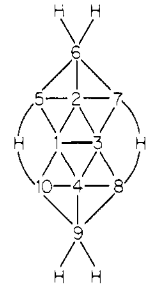
the equivalent C–B positions, giving the pattern



which corresponds to the known structure[19] of $B_{10}H_{14}$ with the standard numbering system in place. It should be clear that no such deduction is possible from the 1-D spectrum alone.

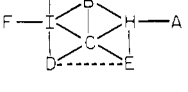
A corresponding approach to the structure of $B_{10}H_{14}^{2-}$ (Figure 2) with the peaks labeled similarly left to right yields the diagram



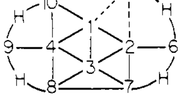


in which the placement of the bridging hydrogen atoms is dictated by the C_{2v} symmetry evident from the spectrum, and the BH_2 groups at the 6, 9 positions are identified from the triplet resonance in the proton-coupled spectrum.[22]

An example of a low-symmetry structure is given by 5-$[C_5(CH_3)_5]CoB_9H_{13}$, whose 1-D spectrum consists of nine peaks of equal area (Figure 13). Once again labeling the peaks alphabetically from left to right, the couplings revealed in the 2-D spectrum yield the connectivity pattern



where the D–E connection must be assumed, since peak overlap prevents observation of a cross peak. Placement of bridging hydrogen atoms on the edges of the nido framework, and filling in the "hole" in the boron skeleton with cobalt, yields a $B_{10}H_{14}$-like structure that conforms to the crystallographically determined geometry.[34a]



It is not necessary to be able to assign all the resonances in a spectrum in order to deduce a unique cage structure. For example, in the spectrum of 1,7-$C_2B_{10}H_{12}$ (Figure 4) the assignment of the B(9, 10) and B(5, 12) peaks is ambiguous, but the only geometry that satisfies both the 2-D coupling information and the electron-count requirement of a closed (icosahedral) framework is the 1, 7 structure shown in the figure. A similar situation obtains for the 1, 2 isomer (Figure 3). Given only the 1-D spectra, no such conclusions could be drawn, and the two isomers could be distinguished only via X-ray crystallography.

Acknowledgment. This research was supported by the National Science Foundation, Grant CHE 81-19936. Purchase of the NT-360 NMR spectrometer system was made possible in part via a major instrumentation grant from the National Science Foundation.

Registry No. $B_{10}H_{14}$, 17702-41-9; $B_{10}H_{14}^{2-}$, 12430-39-6; 1,2-$C_2B_{10}H_{12}$, 16872-09-6; 1,7-$C_2B_{10}H_{12}$, 16986-24-6; *nido*-2,3-$(C_2H_5)_2C_2B_4H_6$, 80583-48-8; *nido*-$[2,3\text{-}(C_2H_5)_2C_2B_4H_5]^-$, 83096-08-6; μ-μ'-$Hg(B_5H_8)_2$, 70850-80-5; μ-(4,5)-$HgCl[1,2,3\text{-}C_5(CH_3)_5Co(CH_3)_2C_2B_3H_4]$, 76081-90-8; *nido*-1,2,3-$[C_6(CH_3)_6]Fe(C_2H_5)_2C_2B_3H_5$, 87862-00-8; 6-$[C_5(CH_3)_5]CoB_9H_{13}$, 43061-99-0; 6-$[C_5(CH_3)_5]CoB_9H_{13}$, 80145-59-1; 2-$(C_5H_5)CoB_9H_{13}$, 68457-40-9; 5-$[C_5(CH_3)_5]CoB_9H_{13}$, 87862-01-9.

Gas-Phase Protonation of Five-Membered Heteroaromatic Rings by $^3HeT^+$ Ions. A Model Reaction for a Theoretical Approach to Heteroaromatic Reactivity[1]

Giancarlo Angelini, Giuseppe Laguzzi, Cinzia Sparapani, and Maurizio Speranza*

Contribution from the Istituto di Chimica Nucleare del C.N.R., Area della Ricerca di Roma, C.P. 10, Rome, Italy. *Received March 23, 1983*

Abstract: The results of a study of the reactions of the powerful Brønsted acid, the $^3HeT^+$ ion from the β decay of molecular tritium, with gaseous pyrrole, *N*-methylpyrrole, furan, and thiophene are reported. In all the systems investigated, the tritiated heteroaromatic substrate is the major product, and it is accompanied in the case of furan by very minor amounts (ca. 3%) of tritiated crotonaldehyde. The nature and the yields of the products, and their intramolecular tritium distribution, suggest that the gas-phase protonation reaction on simple five-membered heteroaromatics is regulated by factors related to the electrostatic interactions established within the encounter pair. A close correspondence exists between the gas-phase protonation results and recent theoretical and experimental evidence concerning related substitution processes.

First insight into the behavior of five-membered heteroaromatics toward charged electrophiles in the gas phase was recently allowed by the application of a radiolytic technique[2] that, unlike most conventional mass spectrometric approaches, provides direct information about the site of attack in the heterocyclic molecule and the structure of the resulting ionic intermediate(s). The available radiolytic data indicate that the behavior of a free heteroaromatic molecule toward an alkylating reactant is frequently quite different from that in solution, where solvation and ion pairing may dramatically modify the intrinsic properties of the substrate.[3] Thus, simple heteroaromatics, such as pyrroles

---

(1) Gas-Phase Heteroaromatic Substitution. 5. For part 4, see: Margonelli, A.; Speranza, M. *J. Chem. Soc. Perkin Trans. 2* **1983**, 1491–1497.

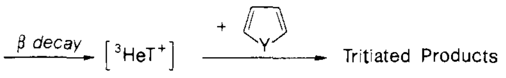
(2) For comprehensive reviews on the radiolytic technique, see: (a) Ausloos, P. *Annu. Rev. Phys. Chem.* **1966**, *17*, 205–236. (b) Ausloos, P. *Progr. React. Kinet.* **1969**, *5*, 113–179. (c) Ausloos, P.; Lias, S. G. "Ion-Molecule Reactions"; Franklin, J. L., Ed.; Plenum Press: New York, 1972. (d) Cacace, F. "Kinetics of Ion-Molecule Reactions"; Ausloos, P., Ed.; Plenum Press: New York, 1979. (e) Speranza, M. *Gazzetta* **1983**, *113*, 37–60.

(3) (a) Speranza, M. *J. Chem. Soc., Chem. Commun.* **1981**, 1177–1178. (b) Angelini, G.; Sparapani, C.; Speranza, M. *J. Am. Chem. Soc.* **1982**, *104*, 7084–7091. (c) Angelini, G.; Lilla, G.; Speranza, M. *Ibid.* **1982**, *104*, 7091–7098. (d) Part 4, see ref 1.

0002-7863/84/1506-0037$01.50/0

1 and **2**, furan (**3**), and thiophene (**4**), as well as benzene and toluene display essentially the same reactivity toward $CH_3FCH_3^+$ and $t\text{-}C_4H_9^+$ ions in the gas phase. In addition, substitution predominantly occurs at the β positions of pyrroles **1** and **2**, at the oxygen of furan (**3**), and at the S and α carbons of thiophene (**4**). All these results were tentatively unified in a single interpretation pointing to the most attractive electrostatic interactions within the ion–heteroaromatic encounter pair as a major factor governing site selection in gas-phase substitution reactions. Accordingly, alkylation is favored at the unsubstituted positions of the heteroaromatic ring with the highest value of the negative net charge.[4] However, other factors, which may be related to the specific nature of the ionic reactant, seem operative in gas-phase heteroaromatic alkylations. For instance, $CH_3FCH_3^+$ and, especially, $t\text{-}C_4H_9^+$ ions preferentially attack the C_α centers of furan (**3**) rather than its C_β carbons, in spite of the fact that these exhibit a greater negative net charge.[4g-i] A plausible explanation can be found in the particular structure of the ionic reactant, which may be able to "chelate" furan,[5] i.e., to establish preliminary interactions with its most attractive site (the oxygen atom), before attacking the most accessible carbon center (one of the adjacent C_α atoms).

In this view, it should be desirable to extend the investigation of the heteroaromatic reactivity toward an ionic electrophile without "chelating" properties. The best candidate appears to be the $^3HeT^+$ ion, which can be conveniently generated in the gas phase by β decay in T_2 molecules.[2d,e,6] A further advantage of the method is the possibility of generating the ion in the absence of any counterion. This fact, coupled with the recognition of $^3HeT^+$ as the ideal positive point charge of theoretical investigation of heteroaromatic reactivity, makes reaction 1 the best experimental ground against which theoretical predictions can be adequately gauged.



(1)

Y = NH (**1**); NCH_3 (**2**); O (**3**); S (**4**)

Experimental Section

Reagents. The gaseous $^3HeT^+$ reagent was generated in the presence of the heteroaromatic substrate by use of a technique based on the decay of molecular tritium, under conditions which excluded the interference of radiolytic labeling processes.[6] Gaseous tritium was obtained from the Radiochemical Centre, Amersham, England, with a stated T_2 content of 98 mol %, the major impurity being HT and ^3He. The heteroaromatic substrates together with 1 mCi of T_2 and a small amount of O_2 (2 torr) were introduced into evacuated Pyrex vessels (ca. 200 mL) equipped with a break seal. Variable amounts of benzene were added in the competition experiments, together with a powerful proton trap (NMe_3), when required. The gaseous samples were stored at room temperature in the dark for 6–12 months, the pressure of the aromatic substrate(s) being adjusted from 0.5 to 5 torr.

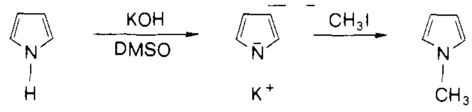
Product Analysis. The tritiated products formed from the attack of $^3HeT^+$ on the substrate(s) were analyzed by radio gas chromatography using a heated Berthold flow-ionization chamber connected to a gas chromatograph. The relative yields of the products were evaluated from the ratio of the areas of their radiochemical peaks to the area of the tritiated parents, suitable corrections being made for changes in the flow rate of the carrier gas. The following columns were used: (i) 3-m 10% Carbowax 20M on 2% KOH treated 80/100 mesh Chromosorb W, operated at 170 °C, for pyrroles **1** and **2**; (ii) 5-m 10% Carbowax 20M on 80/100 mesh Chromosorb W, operated at 70–130 °C (2 °C/min), for furan **3**, and at 95 °C, for thiophene **4**.

Determination of the Tritiated Substrates. In order to measure the absolute yields of the labeled substrates, the major products, and to obtain samples of high radiochemical purity, as required by the degradation procedures described in the next paragraphs, the sealed ampules were cooled with liquid nitrogen, their break seals were ruptured, and known amounts of the appropriate inactive heteroaromatic (and benzene in the competition runs) were added at once. The mixtures were allowed to warm to room temperature, thoroughly mixed, and outgassed to remove most of the unreacted T_2, and the crude substrates were purified to constant molar activity by preparative gas chromatography. The columns used were the same employed in the radio gas chromatographic analyses.

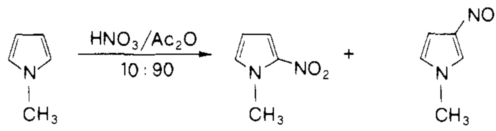
The radioactivity of the purified compounds was determined with a Packard 460C Tri-Carb Liquid Scintillation Spectrometer. The yields were calculated by dividing the activity contained in each labeled product by the total activity of the $^3HeT^+$ ions formed in the gaseous system during the storage period.

Preparation of Substituted Derivatives for the Determination of the Tritium Distribution in the Heteroaromatic Compounds. The replacement of H atoms bound to various ring positions of the heteroaromatic compounds, followed by measurement of the corresponding decrease of the molecular activity, was used to determine the tritium distribution. Substitution reactions were chosen to minimize the danger of tritium losses or redistribution due to unwanted isotopic exchange or scrambling processes. To this purpose, partially or fully deuterated heteroaromatic substrates were prepared according to established procedures and submitted to suitable substitution process. Alternatively, complementary information was obtained by using deuterated reactants. Any conceivable deuterium atom loss, incorporation, or scrambling during the substitution process was followed by conventional NMR analysis.

Pyrrole and *N*-Methylpyrrole. Pyrrole-*1-d* and -d_5 and isomeric pyrrole-d_4 were prepared by H/D exchange of pyrrole by 0.1 N DCl/D_2O. The corresponding N-methylated derivative was obtained following procedure 2:[7] NMR analysis revealed that no modification of the content and the position of the D atoms formerly located on the C atoms of the pyrrole takes place during the N-methylation process. The resulting deuterated *N*-methylpyrroles, as well as those arising from an indipendent CF_3COOD/D_2O exchange route on **2**, were submitted to nitration via process 3:



(2)



(3)

Isomeric *N*-methyl-2-nitro- and *N*-methyl-3-nitropyrroles were resolved and purified on a silica gel chromatographic column. The recovered nitration derivatives displayed a D atom distribution slightly different from the original one. In particular, an average D atom loss is observed for both nitration isomers ranging around 18 ± 6%.

The above procedures (eq 2 and 3) were followed to determine the T atom distribution in pyrrole, after correction for the label loss during nitration 3. In this connection, it should be considered that the actual uncertainty in the ring T distribution of pyrrole is much lower than the extent of label loss in eq 3 (18 ± 6%), since this extent is almost equal for both nitration isomers and, therefore, it tends to cancel out. Nitration 3 was used to establish the T distribution in *N*-methylpyrrole (**2**) as well. Pernitration of the resulting isomeric *N*-methylnitropyrroles (eq 4)[8] was employed to determine the T content in the methyl group of the substrate. Pyrrole-d_5 and *N*-methylpyrrole-d_4 were also used to verify the possibility of label loss to the glassy walls of the reaction vessel during the decay time. To this aim, a suitable amount of the deuterated pyrroles has been

---

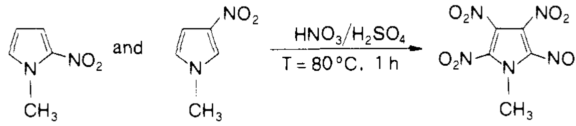
(4) (a) Abronin, I. A.; Belenkii, L. I.; Gol'dfarb, Ya. L. "New Trends in Heterocyclic Chemistry"; Elsevier, North Holland: Amsterdam, 1979. (b) Ridd, J. *Phys. Methods Heterocycl. Chem.* **1971**, *4*, 55–120. (c) Jones, R. A.; Bean, G. P. "The Chemistry of Pyrroles"; Academic Press: New York, 1977. (d) Catalan, J.; Yanez, M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 479–482. (e) Palmer, M. H.; Gaskell, A. J. *Theor. Chim. Acta* **1971**, *23*, 52–58. (f) Kramling, R. W.; Wagner, E. L. *Ibid.* **1969**, *15*, 43–56. (g) Hermann, R. B. *Int. J. Quantum Chem.* **1968**, *2*, 165. (h) Preston, H. J. T.; Kaufman, I. J. *Int. J. Quantum Chem. Symp.* **1973**, *No. 7*, 207–213. (i) Kaufman, I. J.; Preston, H. J. T.; Kerman, E.; Cusachs, L. C. *Ibid.* **1973**, 249–260. (j) Gelius, V.; Roos, B., Siegbahn, P. *Theor. Chim. Acta* **1972**, *27*, 171–185. (k) Bernardi, F.; Bottoni, A.; Mangini, A. *Gazzetta* **1977**, *101*, 55–60.

(5) For examples of "chelating" ionic electrophiles, see: (a) Attinà, M.; Cacace, F.; Ciranni, G.; Giacomello, P. *J. Chem. Soc., Perkin Trans. 2* **1978**, 891–895. (b) Attinà, M.; Cacace, F.; Ciranni, G.; Giacomello, P. *J. Am. Chem. Soc.* **1977**, *99*, 5022–5026. (c) *Ibid.* **1977**, *99*, 4101–4105. (d) Attinà, M.; Cacace, F.; Ciranni, G.; Giacomello, P. *J. Chem. Soc., Chem. Commun.* **1976**, 466–467. (e) Chatfield, D. A.; Bursey, M. *J. Am. Chem. Soc.* **1976**, *98*, 6492–6495.

(6) Cacace, F. *Adv. Phys. Org. Chem.* **1970**, *8*, 79–149.

(7) (a) Patterson, J. M. *Synthesis* **1976**, 281–304. (b) Heaney, H.; Ley, S. V. *J. Chem. Soc., Perkin Trans. 1* **1973**, 499.

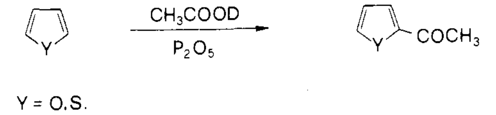
(8) Doddi, G.; Mencarelli, P.; Razzini, A.; Stegel, F. *J. Org. Chem.* **1979**, *44*, 2321–2323.



(4)

introduced into a glassy bulb, identical with those used for the decay systems, together with the usual additives (O_2, benzene, etc.). After 6 months, the pyrrole has been recovered and purified by preparative GLC on the following columns: (i) l-m 20% E-301 Silicone Oil on Chromosorb W 60/80 mesh, T = 60 °C; (ii) 3-m 10% Carbowax 20M on 1% KOH treated Chromosorb W 60/80 mesh, T = 100 °C; (iii) 3-m 20% diisodecyl phthalate on Chromosorb W 60/80 mesh, T = 90 °C. The obtained pyrrole (or N-methylpyrrole) displayed no isotopic exchange or loss during the decay time, according to NMR analysis.

Furan and Thiophene. Acetylation (reaction 5) of furan and thiophene[9] was employed to determine the extent of α tritiation in both substrates. The possibility of label exchange with the reaction environment



(5)

during acetylation was excluded by using CH_3COOD. The acetylated derivative was resolved and purified by preparative GLC on a 3-m 1:1 Bentone 34–diisodecyl phthalate column, operated from 60 °C to 140 °C (25 °C/min). The tritium content of the β positions of the substrates was determined by difference.

Chemical Ionization Mass Spectrometric Experiments. The CIMS experiments were performed on a Micromass VG 7070F mass spectrometer. The materials used were ultra-high-pure D_2 and isobutane gases obtained from Matheson Co. and 99.5 mol % C_6D_6 from Fluka AG. Gaseous mixtures of D_2 (or i-C_4H_{10}):C_6H_6 (or C_6D_6):heteroaromatic in the ratios 1:5 × 10^{-4}:5 × 10^{-4}, prepared in 1-L Pyrex bulbs, were allowed to bleed into the heated (T = 200 °C) source of the mass spectrometer through a metering needle valve. The source pressure (ca. 1 torr) was measured with a Bourdon-type mechanical gauge inserted in place of the direct introduction probe.

Results

The yields of the tritiated products from the gas-phase attack of $^3HeT^+$ on pyrrole (**1**), N-methylpyrrole (**2**), furan (**3**), and thiophene (**4**) are listed in Table I. The relatively large errors of the absolute values reflect the large uncertainty associated with the measurement of the absolute activity of the molecular tritium introduced into the reaction vessels to generate the $^3HeT^+$ electrophile. From the data in the Table I, it is apparent that the combined activity of the reaction products identified fails to account for 100% of the activity of the $^3HeT^+$ reagent. The difference, particularly large in the tritonation of pyrrole and furan, may arise from the formation of labeled compounds (e.g., HT) not discernible from that originally contained in the starting T_2 sample. Another possible activity sink could be the formation of labeled products not detectable by radio gas chromatography, such as high-boiling polymeric materials, and all the substances containing easily exchangeable T atoms. In this connection, it should be observed that furan is the only substrate generating an open-chain tritiated product, i.e., 3% of crotonaldehyde.

The relative rates of formation of the tritiated products were determined by allowing T_2 to decay in systems containing a gaseous mixture of the appropriated heteroaromatics and a reference compound, i.e., benzene, in various molar ratios. Occasionally, comparable amounts of an efficient ion trap, such as NMe_3, were added.

The distribution of tritium in the labeled heteroaromatics formed in the decay systems is given in Table II. Each value is the average of several determinations of the products from a given experiment, at least two separate reaction mixtures being analyzed for each substrate.

Table I. Absolute and Relative Yields of Products Recovered in $^3HeT^+$/Heteroaromatic and $^3HeT^+$/Heteroaromatic/Benzene Systems

system composition[a]			absolute yields,[b] %	yield relative to benzene,[b] k_S/k_B
heteroaromatic substrate	benzene	NMe_3		
pyrrole (1)			41	
pyrrole (0.4)	0.6		45	50
pyrrole (0.5)	0.5		35	30
pyrrole (0.25)	0.25	0.5	26	3
N-methylpyrrole (1)			50	
N-methylpyrrole (0.7)	0.3		52	30
N-methylpyrrole (0.5)	0.5		56	6
N-methylpyrrole (0.25)	0.25	0.5	44	2
furan (1)			37	
furan (0.5)	0.5		49	0.7
furan (0.1)	0.9		48	0.8
furan (0.25)	0.25	0.5	26	1.5
thiophene (1)			78	
thiophene (0.5)	0.5		68	0.5
thiophene (0.25)	0.25	0.5	13	0.7

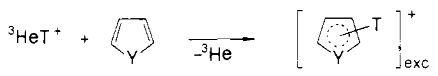
[a] System composition expressed as the molar fraction of each individual component. The total pressure ranges from 0.5 to 5 torr. All systems contained 2 torr of oxygen and ca. 1 mCi of T_2. [b] Standard deviation of data, ca. 15%.

Table II. Percentage of Tritium in the Ring Positions of the Heteroaromatic Products

system composition	% N	% α	% β	β/α ratio
pyrrole	18	37	45	1.2
pyrrole/benzene	25	35	40	1.1
N-methylpyrrole	4	40	56	1.4
N-methylpyrrole/benzene	2	39	59	1.5
furan		38	62	1.6
furan/benzene		34	66	1.9
thiophene		82	18	0.2
thiophene/benzene		62	38	0.6

Discussion

The reagent responsible for the tritonation of the substrates, the $^3HeT^+$ ion, is formed in the ground state in ca. 95% yield from β decay of T_2 (eq 1).[10] The $^3HeT^+$ ion is a very strong Brønsted acid ($\Delta H_f^\circ \simeq$ 320 kcal mol^{-1}),[11] whose ability to tritonate exothermically gaseous organic molecules has been demonstrated.[6] The mechanism suggested for the formation of the tritiated products is analogous to that formulated for the reactions of $^3HeT^+$ with other aromatic substrates,[12] and it involves the exothermic attack of the electrophile on the gaseous substrate with formation of an excited heteroarenium ion [I] (eq 6).[13] If not stabilized



(6)

[I]

---

(9) Hartough, H. D.; Kosak, A. I. *J. Am. Chem. Soc.* **1947**, *69*, 3098–3099.

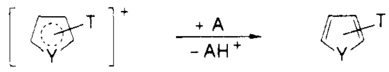
(10) (a) Snell, A. M.; Pleasonton, F.; Leming, H. E. *J. Inorg. Nucl. Chem.* **1957**, *5*, 112. (b) Wexler, S. *Ibid.* **1959**, *10*, 8.

(11) Chupka, W. A.; Russel, M. E. *J. Chem. Phys.* **1968**, *49*, 5426.

(12) (a) Cacace, F.; Caronna, S. *J. Am. Chem. Soc.* **1967**, *89*, 6848–6854. (b) Cacace, F.; Perez, G. *J. Chem. Soc. B* **1971**, 2086–2089. (c) Cacace, F.; Cipollini R.; Ciranni, G. *Ibid.* **1971**, 2089–2092.

(13) The enthalpy change of proton transfer reaction 6 can be computed from the proton affinity (PA) of He, taken as ca. 44 ± 4 kcal mol^1 (Vedeneyev, V. I.; Gurvich, L. V.; Kondrat'yev, V. N.; Medvedev, V. A.; Frankevich, Ye. L. "Bond Energies, Ionization Potentials, and Electron Affinities"; E. Arnold Publishers: London, 1966), and those of pyrrole (PA(**1**) = 213 kcal mol^{-1} (ref 14); PA(**2**) = 220 kcal mol^{-1} (ref 14); PA(**3**) = PA(**4**) = 196 kcal mol^{-1} (ref 15); PA(benzene) = 183.4 kcal mol^{-1}) (ref 16). The relevant $-\Delta H^\circ$ values are (in kcal mol^{-1}) ca. 169 (**1**), ca. 176 (**2**), ca. 152 (**3** and **4**), and 139 (benzene).

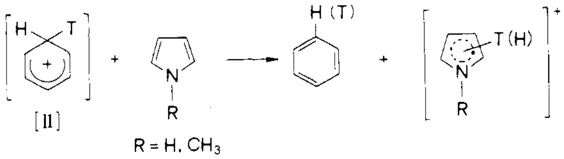
by collision with the gaseous components of the mixture, the intermediate [I] can decompose into smaller fragments, along energetically allowed pathways. The stabilized heteroarenium ions eventually lose a proton to a suitable acceptor (the substrate itself or a NMe_3 molecule, when present) giving rise directly to the tritiated substrate, the major product in all the systems investigated (eq 7). On the reasonable assumption that the yields of the labeled heteroaromatics reflect the fraction of the excited tritonated species that escapes fragmentation, the results confirm and extend earlier observations on the high stability of arenium intermediates in the gas phase. In fact, the absolute yields of tritiated heteroaromatics, ranging from 37 to 78%, are fully comparable with those of toluene (50–60%) and other aromatics, measured under similar conditions.[12]



(7)

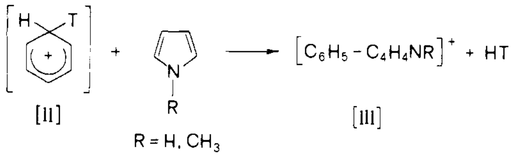
The relatively low yield observed in the case of furan (37%; Table I) may be attributed to the efficient competition between the n electrons and the ring π electrons of the substrate for the gaseous electrophile. Such competition is favored by the high electron density on the oxygen of furan[4] and would lead to the formation of an excited oxonium ion, in addition to the heteroarenium intermediate [I]. The O-tritonated intermediate may follow several reaction pathways, including ring opening and triton loss to a suitable acceptor.[17] Occurrence of this process in furan is suggested by the formation of small yields (ca. 3%) of crotonaldehyde. A similar process appears much less pronounced in the case of thiophene, as demonstrated by the higher absolute product yield (78%) and by the lack of ring-opening derivatives. For pyrroles, appreciable N-tritonation takes place increasing from **2** to **1**, as shown by the yield of the N-substituted derivatives (Table II). The relatively high product yields (41 and 50%) and the lack of ring-opening derivatives are due to the presence on the N atom of pyrroles of a suitable leaving group (H or CH_3), which allows a displacement route prevented in the case of furan.

Competition experiments, based on the reactions of $^3HeT^+$ ions with gaseous heteroaromatic/benzene mixtures, carried out under the same conditions employed for the pure heteroaromatic systems, allow the relative rate of $^3HeT^+$ ion attack on these substrates to be determined. The relevant data, reported in Table I, appears rather sensitive to the composition of the system and the presence of a powerful ion trap, such as NMe_3. In particular, the apparent k_S/k_B values from pyrrole **1** and **2**/benzene systems are much higher than those measured in the presence of NMe_3 (from 3 to 17 times) and very sensitive to the molar ratio of the competing substrates. The reverse is true in the case of furan and thiophene. The intermolecular triton transfer from tritonated benzene to pyrroles, whose extent is minimized in the presence of NMe_3, may be in part responsible for the considerable apparent k_S/k_B values. It is evident, however, that eq 8 cannot be the only intermolecular process involving [II], since, owing to its symmetry, the resulting apparent k_S/k_B would never exceed ca. 7, for pyrrole (**1**), and 5, for *N*-methylpyrrole (**2**).[18]



(8)

The much greater k_S/k_B values, measured in the competition experiments with pyrroles in the absence of NMe_3, must therefore be ascribed to some additional intermolecular process leading to the disappearance of tritonated benzene [II]. A conceivable route may arise from the ability of [II] to add to pyrroles via path 9, a process that has been observed in the source of a mass spectrometer.



(9)

When the D_2 CI mass spectra of a 1:1 = pyrrole/benzene (0.1 mol %) mixture were recorded at pressures around 1 torr and at the ion-source temperature of 200 °C, formation of a high-order ion at masses corresponding to species [III], with ca. 70% deuterium incorporation, is observed. The analogous product $[C_4H_3NRC_4H_4NR]^+$ conceivably arising from addition of [I] to its neutral parent is absent.

In principle, species [III] might also be formed by reaction between protonated pyrrole [I] and benzene. To check this possibility, the D_2 CIMS of a 1:1 = pyrrole/C_6D_6 mixture (0.1 mol %) was carried out. In this case, species [III] retains mostly five D atoms (ca. 80%), indicating that its parent adduct prefers to lose a D_2 rather than a HD molecule (<20%). This evidence is only consistent with an extensively scrambled $C_6H_6D^+$ ion being the major precursor of species [III], via the addition-elimination process 9 involving loss of a hydrogen molecule from the parent ion. The CIMS experiments have been repeated by using *t*-$C_4H_9^+$ as ionic reactant to limit the excitation energy of [II]. Formation of [III] is observed, whereas related species are not formed from furan and thiophene.

Intermolecular pathways 8 and 9, as well as secondary fragmentation and ring-opening processes, are efficiently inhibited in the decay competition experiments carried out in the presence of NMe_3, as demonstrated by the considerably lower k_S/k_B values (ca. 3 from **1** and ca. 2 from **2**).

The limited propensity of [II] to condense with furan and thiophene, observed in the CIMS experiments, is reflected in the similar values of the apparent k_S/k_B ratios measured in the competition experiments (Table I). Contrary to pyrroles, furan and thiophene display k_S/k_B ratios that tend to slightly increase in the presence of NMe_3 (from 0.7 to 1.5 (**3**) and from 0.5 to 0.7 (**4**)). This behavior suggests that the effect of the base in intercepting intermolecular processes is overwhelmed by its ability in minimizing secondary fragmentation and ring-opening processes in [I] particularly pronounced in the case of furan.

Some information on the nature of the tritonated intermediate [I] from eq 6 can be obtained from the distribution of the tritium within the labeled heteroaromatics, in the reasonable hypothesis that the distribution itself reflects the original sites of the $^3HeT^+$ attacks.[12a,19] The data of Table II clearly indicate that the $^3HeT^+$ ion attacks preferentially the β carbons of pyrroles and furan and the α carbons of thiophene. Substantial attack on the oxygen of furan cannot be excluded as well. Such findings are in substantial agreement with earlier conclusions concerning the directive properties of the same substrates in related gas-phase electrophilic substitutions.[3] Concerning furan, the present data demonstrate that a monodentate electrophile, such as $^3HeT^+$, is preferentially directed toward the ring sites of the substrate with the highest

---

(14) (a) Devlin, J. L., III; Wolf, J. F.; Taft, R. W.; Hehre, W. J.; McIver, R. T., Jr.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 7162–7163. (b) Aue, D. H.; Webb, H. M.; Bowers, M. T. *Ibid.* **1972**, *94*, 4726–4728.

(15) Houriet, R.; Schwarz, H.; Zummack, W.; Andrade, J. G.; Schleyer, P. v. R. *Nouv. J. Chim.* **1981**, *5*, 505–509.

(16) Lau, Y. K.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 7452–7453.

(17) Apart from the substrate itself, the triton may be lost to the walls of the reaction vessel, or to traces of nucleophiles invariably present or radiolytically formed in the gaseous decay system.

(18) Values arrived at by assuming that the k_S/k_B values, measured in the presence of NMe_3 (k_S/k_B = 3 (**1**); 2 (**2**)), reflect the actual intermolecular selectivity of the $^3HeT^+$ ion and that complete H or T transfer from [II] to the heteroaromatic substrate (eq 8) takes place at the same rate.

(19) Owing to the large exothermicity of the tritonation process (ref 13), it cannot be a priori excluded occurrence of partial tritium scrambling within the charged adducts [I]. It must be pointed out, however, that protium rather than tritium scrambling should take place in [I] on account of the large kinetic isotope effect. Furthermore, scrambling should be efficiently prevented by collisional quenching of the excited intermediate [I] and by its fast neutralization by proton transfer to a suitable base (the substrate itself or NMe_3).

negative net charge (the C_β and, possibly, O atom),[4g–i] thus confirming the view that the *intrinsic* positional selectivity of simple heteroaromatic toward powerful ionic electrophiles is governed by factors strictly related to the charge distribution developed in the encounter pair.

The preferred O and C_α substitution previously observed when the gaseous electrophile is a bidentate ion ($CH_3FCH_3^+$ or t-$C_4H_9^+$) is therefore attributed to a preliminary "hydrogen-bond-like" interaction (prevented in $^3HeT^+$) between the hydrogens of the electrophile and the hard site (the n electrons) of furan, which would favor α substitution.[20]

The available gas-phase experimental results are in good agreement with recent semiempirical calculations of the attractive potentials generated by the interaction of an isolated molecule of **1–4** and a positively charged electrophile.[21b] It should be emphasized that the agreement is complete when the experiments are carried out under conditions as close as possible to the ideal ones of theoretical calculations. Thus, use of a free unsolvated heteroaromatic molecule and the gaseous electrophile $^3HeT^+$ (which can be reasonably assumed as a positive point charge) shows that the aforementioned theoretical approach correctly predicts site selectivity in heteroaromatic substitution, without requiring those forced assumptions necessary to provide a theoretical justification for data obtained in solution, i.e., under conditions totally different from those pertaining to the theoretical approach itself.[21]

Conclusions

The essential features of gas-phase electrophilic substitution on simple five-membered heteroaromatics are exhibited by the gas-phase reaction of $^3HeT^+$ ions, formed from the β decay of molecular tritium, with pyrrole, *N*-methylpyrrole, furan, and thiophene. The low substrate discrimination of the $^3HeT^+$ ion, comparable with that observed in related substitutions with gaseous electrophiles, such as $CH_3FCH_3^+$ and t-$C_4H_9^+$,[3] can be explained by the exceedingly high reactivity of the unsolvated ionic reactant. The *intrinsic* directive properties of simple heteroaromatics toward powerful gaseous electrophiles, especially $^3HeT^+$, are found to correlate well with theoretical predictions based upon the molecular electrostatic potential established in the encounter pair.[21] In particular, β (and Y) substitution predominantly takes place in furan and pyrrole, β attack in *N*-methylpyrrole, and α displacement in thiophene. This kinetic behavior appears in substantial disagreement with the conclusions of related gas-phase ICR investigation based on the behavior of $C_4H_5Y^+$ species after attaining thermodynamic equilibrium.[15,22]

Acknowledgment. The authors wish to express their gratitude to Dr. Arturo Razzini for his interest in the present work and useful suggestions in the preparation of substituted heteroaromatics. Acknowledgment is also due to the Mass Spectrometry Service of the Area della Ricerca di Roma, C.N.R., for running the CIMS experiments.

Registry No. 1, 109-97-7; **2**, 96-54-8; **3**, 110-00-9; **4**, 110-02-1; $^3HeT^+$, 87568-71-6.

---

(20) Pepe, N.; Speranza, M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1179–1186.

(21) (a) Politzer, P.; Weinstein, H. *Tetrahedron* **1975**, *31*, 915–923. (b) Chou, D.; Weinstein, H. *Ibid.* **1978**, *34*, 275–286. (c) Politzer, P.; Donnelly, R. A.; Daiker, K. C. *J. Chem. Soc., Chem. Commun.* **1973**, 617. (d) Bertheir, G.; Bonaccorsi, R.; Scrocco, E.; Tomasi, J. *Theor. Chim. Acta* **1972**, *26*, 101–105.

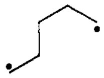
(22) Houriet, R.; Schwarz, H.; Zummack, W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 905–906.

Qualitative Valence Bond Theory and Firestone's Extended Diradical for 1,3-Dipolar Cycloadditions

Richard D. Harcourt* and R. Daniel Little

Contribution from the Department of Physical Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia, and the Department of Chemistry, University of California, Santa Barbara, California 93106. Received April 26, 1983

Abstract: A qualitative valence bond analysis of the nature of Firestone's extended diradical



for the "1,3-dipolar" cycloaddition reaction is provided. It is deduced that the ground state for this species corresponds approximately to a (geometrically) nonsymmetrical transition state for a concerted mechanism for the cycloaddition. It is also deduced that the energy minimum for an electronic excited state lies immediately above this transition state. The excited state does not correlate with the ground states of the reactants or the cycloaddition product. If it is populated, subsequent reaction may lead to H atom abstraction and oxime product formation, as is observed to occur together with cycloaddition, for the thermal reaction of PhCNO with PhCCH. If the transition state for the cycloaddition has a symmetrical geometry, Firestone's cyclo diradical

corresponds neither to the transition state nor to an intermediate, but rather to an entity whose electronic structure lies between that of the transition state and the cycloaddition product. The excited state that lies immediately above the symmetrical transition state is probably not thermally accessible. Regardless of the geometry, a two-step mechanism will pertain if secondary structures, which involve the transfer of at least one electron between the reactants, are dominant after the first transition state has been reached.

The controversy between Huisgen[1] and Firestone[2] concerning the mechanism for 1,3-dipolar reactions—for example, benzonitrile oxide + phenylacetylene (**1**) → 2,5-diphenylisoxazole (**3**)—is longstanding. Whereas Huisgen has postulated that the mech-

0002-7863/84/1506-0041$01.50/0 © 1984 American Chemical Society