influence of the reaction medium (solvation, ion pairing, catalyst, etc.) as the main factor responsible for the reactivity and selectivity features of pyrroles toward electrophilic substitution in solution.

running the CIMS experiments.

Gas-Phase Heteroaromatic Substitution. 3.[1] Electrophilic Methylation of Furan and Thiophene by $CH_3XCH_3^+$ (X = F or Cl) Ions

Giancarlo Angelini, Gaetano Lilla, 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 September 17, 1982

Abstract: A previous radiolytic study on the gas-phase methylation of pyrrole and *N*-methylpyrrole by $CH_3XCH_3^+$ (X = F or Cl) ions, from the γ radiolysis of CH₃X, is extended to furan (**3**) and thiophene (**4**). The mechanism of the substitution and of the subsequent isomerization occurring via intramolecular 1,2 methyl-group shifts is discussed and the *substrate* and *positional* selectivity of the selected electrophilic species evaluated. As for pyrroles, gas-phase $CH_3FCH_3^+$ methylation of furan and thiophene is characterized by a scarce substrate discrimination (k_S/k_B = 1.2 (**3**), 0.8 (**4**)), accompanied by an appreciable positional selectivity toward those substrate positions with the highest negative net charge (O:α:β = 36%:35%:29% for **3**; S:α:β = 19%:43%:38% for **4**). On the contrary, $CH_3ClCH_3^+$ confirms its inherent affinity toward n-type nucleophilic centers by attacking preferentially the heteroatom of **3** and **4**. In light of the previous results concerning $CH_3XCH_3^+$ methylation of pyrroles, it is concluded that gas-phase attack of $CH_3XCH_3^+$ on simple five-membered heteroaromatics is essentially regulated by the electrostatic interaction established within the encounter pair. A close correspondence does exist between this rationalization of the present gas-phase results and recent theoretical predictions.

In the preceding papers of this series, the application of a specifically designed radiolytic technique for the study of heteroaromatic substitution by $CH_3XCH_3^+$ (X = F or Cl) ions in the dilute gas state has been reported.[1] In particular, the *intrinsic* reactivity features of pyrrole (**1**) and *N*-methylpyrrole (**2**) toward gaseous $CH_3XCH_3^+$ ions have been evaluated. $CH_3FCH_3^+$ ions displayed a scarce *substrate* selectivity, coupled with a remarkable *positional* discrimination, in its electrophilic attack on the pyrrolic substrates. In fact, extensive attack on β-carbons of the heterocyclic compound was observed in the gaseous phase in contrast with the evidence available from related substitutions in solution.[2] These findings are in agreement with most advanced theoretical predictions.[3-5] Instead, the $CH_3ClCH_3^+$ ion confirmed its peculiar affinity toward n-type centers[6] by displaying its scarce reactivity

even toward π-electron-rich compounds, such as pyrrole (**1**) and *N*-methylpyrrole (**2**).

1, R = H
2, R = CH₃
3, Y = O
4, Y = S
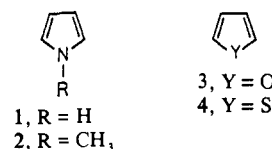
With the aim of confirming the validity of such relationship, the investigation has been now extended to the determination of the reactivity features of $CH_3XCH_3^+$ (X = F or Cl) ions toward other simple five-membered heteroaromatics, containing both n- and π-type nucleophilic sites, i.e., furan (**3**) and thiophene (**4**). It is expected that this study would also lead to the assessment of a unified *intrinsic* reactivity scale for simple heteroaromatics toward the $CH_3XCH_3^+$ ions, which are known to be involved in Friedel–Crafts methylation reactions by methyl halides.[7] It is thereby hoped to provide a simplified model linking gas-phase heteroaromatic substitutions to the related reactions occurring in solution. Interpretation of these results is, in fact, severely hampered by the recognized effects of solvation, ion pairing, catalysts, etc. and the other complicating phenomena related to the reaction environment.[2]

Experimental Section

Materials. Furan, 2-methylfuran, thiophene, 2- and 3-methylthiophenes, and benzene are commercially available from ICN Pharmaceutical, Inc., and Fluka AG. 3-Methylfuran was prepared according to established procedures.[8] Immediately before use, these compounds

(1) Presented in part at the 8th International Congress of Heterocyclic Chemistry, Graz, Austria, Aug 1981. Part 1: Speranza, M. *J. Chem. Soc., Chem. Commun.* **1981**, 1177–1178. Part 2: Angelini, G.; Sparapani, C.; Speranza, M. *J. Am .Chem. Soc.*, preceding paper in this issue.

(2) For comprehensive reviews, see: (a) Marino, G. *Adv. Heterocycl. Chem.* **1971**, *13*, 235–314. (b) Katritzky, A. R.; Lagowsky, J. M. "The Principles of Heterocyclic Chemistry"; Academic Press: New York, 1968. (c) Albert, A. "Heterocyclic Chemistry", 2nd ed., Oxford University Press: New York, 1968. (d) Jones, R. A. *Adv. Heterocycl. Chem.* **1970**, *11*, 383.

(3) (a) Abronin, I. A.; Belenkii, L. I.; Gol'dfarb, Ya. L. "New Trends in Heterocyclic Chemistry"; Elsevier: North-Holland, 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.

(4) (a) Catalan, J.; Yanez, M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1627–1631. (b) Palmer, M. H.; Gaskell, A. J. *Theor. Chim. Acta* **1971**, *23*, 52–58. (c) Kramling, R. W.; Wagner, E. L. *Ibid.* **1969**, *15*, 43–56.

(5) (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**, 617–618. (d) Berthier, G.; Bonaccorsi, R.; Scrocco, E.; Tomasi, J. *Theor. Chim. Acta* **1972**, *26*, 101–105.

(6) (a) Speranza, M.; Pepe, N.; Cipollini, R. *J. Chem. Soc., Perkin Trans 2* **1979**, 1179–1186. (b) Pepe, N.; Speranza, M. *Ibid.* **1981**, 1430–1436. (c) Speranza, M. Angelini, G. *J. Am. Chem. Soc.* **1980**, *102*, 3115–3120. (d) Angelini, G.; Speranza, M. *Ibid.* **1981**, *103*, 3792–3799. (e) *Ibid.* 3800–3806. (f) Colosimo, M.; Bucci, R. *J. Phys. Chem.* **1979**, *83*, 1952–1957.

(7) (a) Olah, G. A. "Halonium Ions"; Olah, G.A., Ed.; Wiley: New York, 1975. (b) Olah, G. A.; DeMember, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 718–720. (c) Olah, G. A.; Melby, E. G. *Ibid.* **1972**, *94*, 6220–6221. (d) Olah, G. A.; Yamada, Y.; Spear, R. *J. Ibid.* **1975**, *97*, 680–681. (e) Peterson, P. E.; Brockington, R.; Vidrine, D. W. *Ibid.* **1976**, *98*, 2660–2661. (f) Olah, G. A.; Donovan, D. J.; Lin, H. C. *Ibid.* 2661–2663.

(8) Sherman, E.; Amstutz, E. D. *J. Am. Chem. Soc.* **1950**, *72*, 2195–2199.
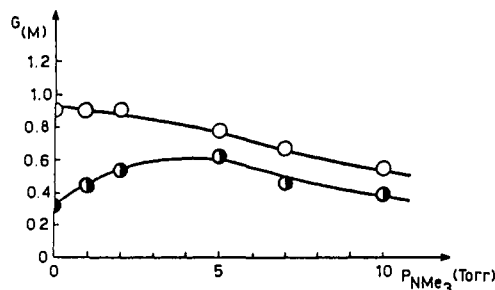
Figure 1. System: CH_3F (740–760 torr) + furan (3) (1.0–2.0 torr) + benzene (1.0–2.0 torr) + O_2 (4 torr). Dependence of the G_M values on the partial pressure of NMe_3 (P_{NMe_3}): (◑) methylfurans 5 and 6; (○) toluene.
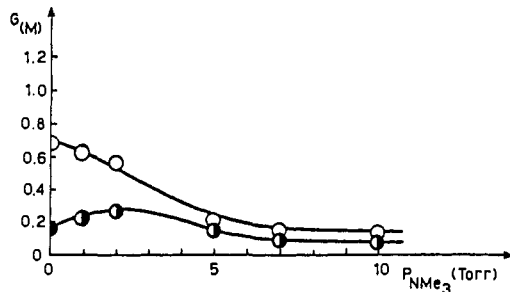
Figure 2. System: CH_3F (740–760 torr) + thiophene (4) (0.4–1.2 torr) + benzene (0.7–0.8 torr) + O_2 (4 torr). Dependence of the G_M values on the partial pressure of NMe_3 (P_{NMe_3}): (◑) methylthiophenes 7 and 8; (○) toluene.

were repeatedly purified by preparative GLC. Their purity was checked by GLC on the same columns employed for the analysis of the reaction mixtures. Methyl fluoride, methyl chloride, oxygen, argon, and trimetylamine (Matheson Co.) were used without further purification.

Procedure. The preparation and irradiation of the gaseous samples were carried out according to experimental techniques described in detail in the preceding papers.[1] Typical experimental conditions were as follows: CH_3X, 20–760 torr; furan or thiophene, 0.4–2 torr; O_2, 4 torr; NMe_3, 0–10 torr; radiation dose, 4.8 Mrd; dose rate, 0.30 Mrd h^{-1}; irradiation temperature, 37.5 °C. Control experiments, carried out at doses ranging from 1 to 10 Mrd, showed that the relative yields of products and their isomeric composition are largely independent of the dose.

The analysis of the irradiation products was performed with a Perkin-Elmer Sigma 3 gas chromatograph equipped with a FID unit. The following columns were used: (a) 8 m 25% dimethylsulfolane on Chromosorb W 60–80 mesh, T_C 40 °C; (b) 9 m 25% silicone oil E 301 on Chromosorb W 60–80 mesh, T_C 70 °C; (c) 5 m 1:1 bentone-34–diisodecyl phthalate mixture at 70 °C. The products were identified by comparison of their retention volumes with those of the authentic standard compounds. Their yields were determined from the areas of the corresponding eluted peaks, using individual calibration curves. The identity of the products was further confirmed by GC–MS, using a Micromass VG 7070 F mass spectrometer. The same instrument was employed for the chemical ionization (CI) experiments, using CH_3X as the reactant gas.

Results

CH_3F Systems. The absolute yields of the methylated products from the gas-phase $CH_3FCH_3^+$ attack on furan and thiophene, measured in competition experiments with benzene as the reference substrate, are reported in Figures 1 and 2, respectively. The yields are expressed as G_M values, i.e., as the number of molecules M produced per 100 eV of energy adsorbed by the gaseous mixture and refer to irradiations carried out at 37.5 °C and to a total dose of 4.8 Mrd (dose rate 0.30 Mrd h^{-1}).[9] The resulting apparent rate constant ratios k_S/k_B as a function of the total pressure of
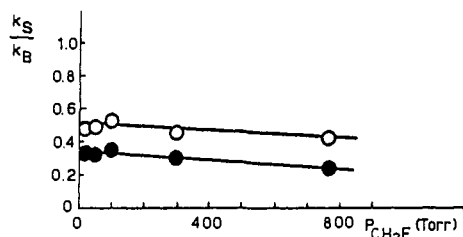
Figure 3. Dependence of the apparent k_S/k_B ratios (see text) on the total pressure of the competition systems: (○) furan (3)/benzene; (●) thiophene (4)/benzene.
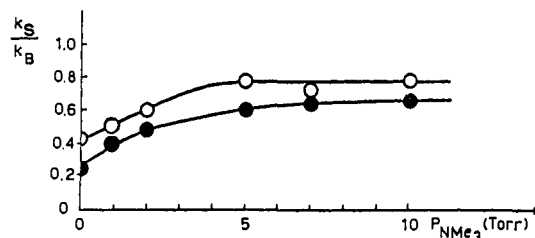
Figure 4. Dependence of the apparent k_S/k_B ratios (see text) on the partial pressure of NMe_3 (P_{NMe_3}) at a total pressure of 760 torr: (○) furan (3)/benzene; (●) thiophene (4)/benzene.

the system and of the NMe_3 concentration are given respectively in Figures 3 and 4. In analogy with the results of $CH_3FCH_3^+$ methylation of pyrroles 1 and 2, dimethylfluoronium ion attack on furan (3) and thiophene (4) gives predominantly the corre-

	Y	R	R_1
3,	O	H	H
4,	S	H	H
5,	O	CH_3	H
6,	O	H	CH_3
7,	S	CH_3	H
8,	S	H	CH_3

sponding methylated derivatives (relative yield over 85%). In the absence of NMe_3, this reaction is accompanied by secondary processes, whose extent ($\simeq 20\%$) appears to be efficiently depressed by the presence of limited amounts (≥ 5 torr) of NMe_3. This is demonstrated by the bell-shaped curves describing the dependence of the yields of methylfurans (5 and 6) (Figure 1) and methylthiophenes (7 and 8) (Figure 2) upon the NMe_3 partial pressure and by the tendency of the relevant apparent k_S/k_B ratios to increase with the base concentration up to a constant value (k_S/k_B = 0.78 (3), 0.65 (4)) for $P_{NMe_3} > 5$ torr. Information on the ionic intermediates formed by attack of $CH_3FCH_3^+$ ions on 3 and 4 is available from the CH_3F CI mass spectra of furan and thiophene (0.6 mol %), recorded at an ion-source temperature of 200 °C and in the pressure range from 0.1 to ca. 1.0 torr. The (M + 15)$^+$/(M + 13)$^+$ ratio (denoting the relative abundance of the condensation adduct ((M + 15)$^+$) vs. the condensation–fragmentation product ((M + 13)$^+$)) is found to be dependent upon the ion-source pressure, as in the case of pyrroles 1 and 2. Thus, the (M + 15)$^+$/(M + 13)$^+$ ratio from 3 decreases from ca. 0.66 at 1.0 torr to ca. 0.10 at 0.1 torr. In the case of 4, it decreases from 0.26 to 0.08 within the same pressure range.

The isomeric composition of the products from $CH_3FCH_3^+$ methylation of furan and thiophene, either neat or in competition with benzene, has been measured under largely different experimental conditions and are reported in Figures 5–12. The relative yields of methylfurans (5 and 6) from 3 are markedly dependent of the total pressure of the system (Figure 5); in fact, the 5:6 yield ratio decreases from 2.5 at 760 torr to ca. 0.8 at 20 torr. Addition of even limited amounts of NMe_3 (2 torr) to the gaseous systems at atmospheric pressure (Figure 6) leads to a significant decrease

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(9) The yields of the methylated products drop to zero when CH_3X (X = F or Cl) is replaced with Ar. This confirms that the products are originated exclusively from the $CH_3XCH_3^+$ ions. The presence of an effective thermal radical scavenger, such as O_2 (4 torr), in the gaseous systems excludes contribution of radical species to the formation of the recovered products.
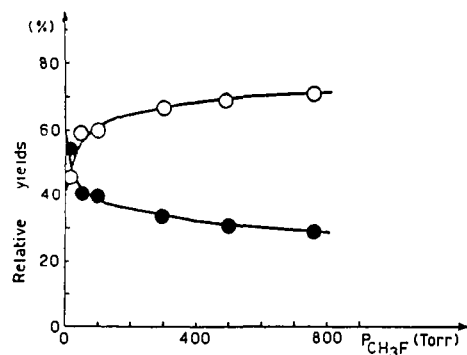
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Figure 5. Relative yields of isomeric methylfurans **5** and **6** from $CH_3FCH_3^+$ attack on furan (**3**) as a function of the total pressure (P_{CH_3F}) of the system in the absence of NMe_3: (O) 2-methylfuran (**5**); (●) 3-methylfuran (**6**).
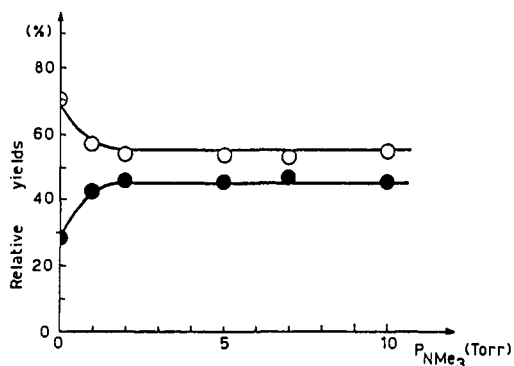
Figure 6. Relative yields of isomeric methylfurans **5** and **6** from $CH_3FCH_3^+$ attack on furan (**3**) at 760 torr as a function of the partial pressure of NMe_3 (P_{NMe_3}): (O) 2-methylfuran (**5**); (●) 3-methylfuran (**6**).
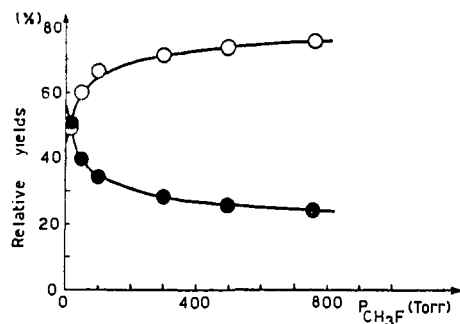
Figure 7. Relative yields of isomeric methylfurans **5** and **6** from furan (**3**) in the competition experiments as a function of the total pressure (P_{CH_3F}) of the system in the absence of NMe_3: (O) 2-methylfuran (**5**); (●) 3-methylfuran (**6**).
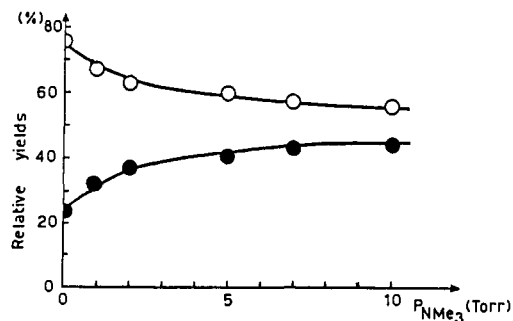
Figure 8. Relative yields of isomeric methylfurans **5** and **6** from furan (**3**) in the competition experiments at 760 torr as a function of the partial pressure of NMe_3 (P_{NMe_3}): (O) 2-methylfuran (**5**); (●) 3-methylfuran (**6**).

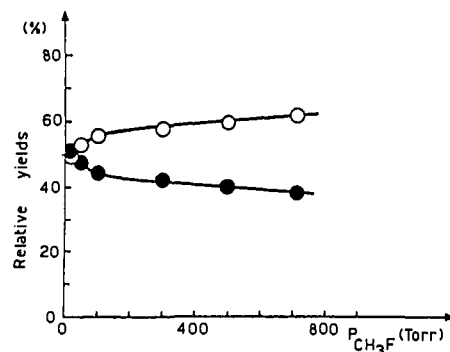**Figure 9.** Relative yields of isomeric methylthiophenes **7** and **8** from $CH_3FCH_3^+$ attack on thiophene (**4**) as a function of the total pressure (P_{CH_3F}) of the system in the absence of NMe_3: (O) 2-methylthiophene (**7**); (●) 3-methylthiophene (**8**).

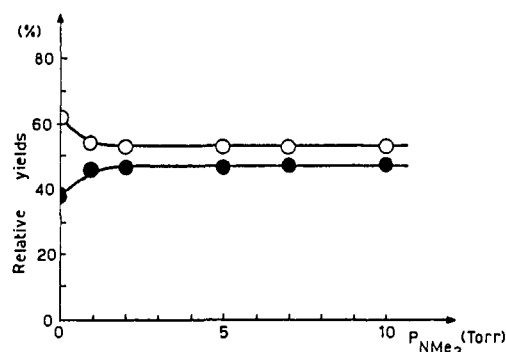**Figure 10.** Relative yields of isomeric methylthiophenes **7** and **8** from $CH_3FCH_3^+$ attack on thiophene (**4**) at 760 torr as a function of the partial pressure of NMe_3 (P_{NMe_3}): (O) 2-methylthiophene (**7**); (●) 3-methylthiophene (**8**).

Figure 11. Relative yields of isomeric methylthiophenes **7** and **8** from thiophene (**4**) in the competition experiments as a function of the total pressure (P_{CH_3F}) of the system in the absence of NMe_3: (O) 2-methylthiophene (**7**); (●) 3-methylthiophene (**8**).

Figure 12. Relative yields of isomeric methylthiophenes **7** and **8** from thiophene (**4**) in competition experiments at 760 torr as a function of the partial pressure of NMe_3 (P_{NMe_3}): (O) 2-methylthiophene (**7**); (●) 3-methylthiophene (**8**).

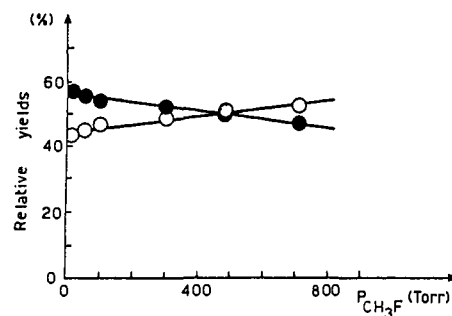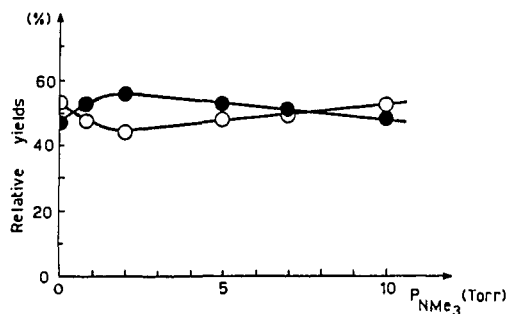of the **5**:**6** ratio to a value of ca. 1.2. This ratio is maintained also at higher NMe_3 concentrations. The same qualitative behavior

is observed in the competition experiments (Figures 7 and 8). A similar situation is found in the isomeric distribution of the methylthiophenes (**7** and **8**) from CH$_3$FCH$_3$$^+$ attack on **4** (Figures 9–12). A constant 53%:47% = **7**:**8** distribution is observed at atmospheric pressure when NMe$_3$ is present (Figure 10); it changes abruptly to 62%:38% in the absence of the amine. The effect of NMe$_3$ on the **7**:**8** ratio is, however, more complex in the competition experiments (Figure 12). At 10 torr of NMe$_3$, a **7**:**8** ratio (= 1.1) is observed, which is the same of that measured in the absence of the benzene competitor (cf. Figures 10 and 12). At lower NMe$_3$ partial pressure, however, the presence of benzene favors formation of **8** with respect to **7**. The **7**:**8** ratio reaches the lowest value of ca. 0.8 at 1–2 torr of NMe$_3$ (Figure 12). The predominance of the α isomer is then restored (**7**:**8** = 1.1), in the absence of NMe$_3$. Finally, the general tendency of the **7**:**8** ratio to decrease at low total pressure is observed (ca. 45%:55% at P_{CH_3F} = 20 torr (Figures 9 and 11)).

CH$_3$Cl Systems. The absolute yields of the methylated products from the gas-phase CH$_3$ClCH$_3$$^+$ attack on furan (**3**) and thiophene (**4**) turn out to be rather low for the reactivity standard of dimethylchloronium ions toward n-type bases.[6] The overall G_M values of the methylated products (**5** and **6**) and (**7** and **8**) range from 0.05 to 0.10 at all system pressures investigated. They decrease by a factor of ca. 5 with the addition of limited amounts (0.3–1.5 mol %) of NMe$_3$. The apparently scarce reactivity of gaseous CH$_3$ClCH$_3$$^+$ toward **3** and **4** is not confirmed by the corresponding CH$_3$Cl CI experiments (ion-source temperature 200 °C; pressure range 0.1–1.0 torr). The relevant result is that the relative ion intensities of the CH$_3$ClCH$_3$$^+$ methylation products ((M + 15)$^+$ and (M + 13)$^+$) from **3** and **4** (0.6 mol %) reach approximately the same levels of those measured in the CH$_3$F CI mass spectra of the same heterocyclic compounds.[10]

A distribution of **5**:**6** = 70%:30% arises from the CH$_3$ClCH$_3$$^+$ attack on furan **3** in the presence of 2–10 torr of NMe$_3$. The **5**:**6** ratio increases in the absence of NMe$_3$ and at 760 torr to reach a value exceeding 10. At lower pressures it slightly decreases. Thiophene **4** is methylated by CH$_3$ClCH$_3$$^+$ at atmospheric pressure in the presence of 10 torr of NMe$_3$, giving a **7**:**8** = 40%:60% distribution. At lower NMe$_3$ concentrations, this ratio appreciably increases to reach a value of ca. 1.3 in the absence of the base. The relative yield of the β isomer **8** slowly increases at pressures below 1 atm and becomes again predominant ($\simeq$53%) at pressures <50 torr. The presence of benzene in the mixtures with **3** or **4** does not significantly modify the results.

In conclusion, the major features of the gas-phase CH$_3$XCH$_3$$^+$ (X = F or Cl) methylation of furan and thiophene can be summarized as follows:

(i) Furan (**3**) and thiophene (**4**), as well as benzene, are efficiently methylated by CH$_3$FCH$_3$$^+$ ions. A comparatively scarce reactivity is observed for radiolytic CH$_3$ClCH$_3$$^+$ ions toward the same substrates, in contrast to the high intensities of the methylation intermediates formed in the CH$_3$Cl CI mass spectra of **3** and **4**.

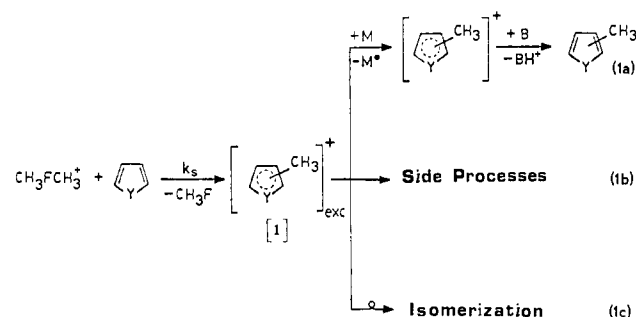(ii) CH$_3$FCH$_3$$^+$ methylation of **3** and **4** is accompanied by collateral parasitic processes that can be inhibited by addition of suitable amounts of NMe$_3$.

(iii) Dimethylhalonium ion attack on furan in the gas phase apparently leads to predominant α substitution under almost all conditions, with the exception of very low (≤20 torr) total pressures.

(iv) On the contrary, predominance of either of methylated isomers of thiophene is regulated by the total pressure of the system, NMe$_3$ concentration, and the presence of the benzene competitor.

(v) The presence of benzene in the CH$_3$F competition experiments with **3** enhances the relative extent of α substitution. Alternatively, the increase of the relative yield of the β isomer

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(10) Furthermore, it should be pointed out that the combined (M + 15)$^+$ + (M + 13)$^+$ ion abundance measured in the CH$_3$Cl CI experiments on **3** and **4** exceeds that arising from the CH$_3$Cl CI mass spectra of **1** and **2** by a factor of 5.

Scheme I

Table I. Methyl Cation Affinities of Various Species^a

species	MCA, kcal mol^{-1}	source
CH$_3$F	44 ± 8	ref 11
CH$_3$Cl	⩾51	ref 11
C$_6$H$_6$	88	ref 6a
NH$_3$	102	ref 6a
NMe$_3$	~140	ref 12
furan	~96	ref 13
thiophene	~109	ref 13

^{a} Methyl cation affinities (MCA) as defined in ref 11.

is observed in the competition experiments with **4**. In the CH$_3$Cl systems, no evident effect of the presence of benzene on the methylated product distribution is observed.

Discussion

Methylation Mechanism. In accordance with the conclusions reached in the preceding paper, the results of the radiolytic and CI experiments suggest that CH$_3$FCH$_3$$^+$ attack on the selected heteroaromatics induces the general reaction pattern outlined in Scheme I. Reaction 1a–c is flanked by the benzene methylation reaction 2 in the competition experiments. Dimethylfluoronium
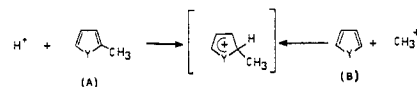

ion attack on **3** and **4** leads to the corresponding methylated intermediate I, which is excited by the exothermicity of its formation process ($\Delta H° = -(50-70)$ kcal mol^{-1}) (see Table I). Collisional stabilization of I, followed by proton transfer to a gaseous base B (e.g., NMe$_3$, or the substrate itself),[14] provides a direct route to the neutral methylated substrate (eq 1a). Al-

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(11) Beauchamp, J. L.; Holtz, D.; Woodgate, S. D.; Patt, S. L. *J. Am. Chem. Soc.* **1972**, *94*, 2798–2807.

(12) Quoted in ref 15 of the preceding paper.

(13) A tentative estimate of the MCA of furan (**3**) and thiophene (**4**) can be arrived at by considering the reactions and by assuming that the proton
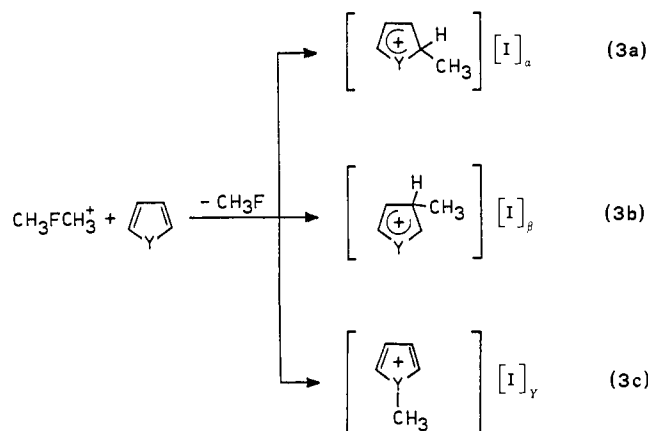

affinity (PA) of A at the ring position bearing the methyl group is very close to that of the corresponding fundamental heteroaromatic B (Devlin, J. L., III; Wolf, J. F.; Taft, R. W.; Hehre, W. J. *J. Am. Chem. Soc.* **1976**, *98*, 1990–1992. Hehre, W. J.; McIver, R. T., Jr.; Pople, J. A.; Schleyer, P.v.R. *Ibid.* **1974**, *96*, 7162–7163), namely, PA(3): 195.5 kcal mol^{-1} (quoted in: Houriet, R.; Schwarz, H.; Zummack, W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 905–906) and PA(4): 205 kcal mol^{-1} (Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976). The $\Delta H_f°$'s of **3** (−8 kcal mol^{-1}) and **4** (28 kcal mol^{-1}) have been taken from Cox and Pilcher (Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970). The $\Delta H_f°$'s of methylfurans ($\simeq$ −15 kcal mol^{-1}) and methylthiophenes ($\simeq$ 20 kcal mol^{-1}) have been calculated from those of the corresponding unsubstituted heteroaromatics by using the group additivity rules (Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976).

(14) Other gaseous bases available to intermediates I and II could be formed from the γ radiolysis of the batch gas.

Electrophilic Methylation of Furan and Thiophene
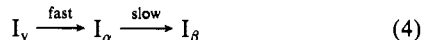
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ternatively, the excited intermediate I may undergo several secondary processes, including isomerization to a more stable structure (eq 1b,c).[15] The competition of the side reactions (1b,c) with the direct methylation channel (1a) appears regulated by the density of the third body M (CH_3F) and by the presence and the concentration of the base B, which eventually neutralizes the ionic intermediates.

Therefore, the initial population of the C-methylated intermediates I emerges directly from the isomeric distribution of the neutral products as measured under kinetically controlled conditions, i.e., formed at 760 torr and in the presence of 10 torr of NMe_3. Under such conditions, the efficient collisional quenching of the excited I and its rapid neutralization by NMe_3 minimize the extent of competing side processes 1b and 1c. This is demonstrated by the constancy of the product distribution (Figures 6 and 10) as well as the apparent k_S/k_B ratio (Figure 4) for $P_{NMe_3} \geq 5$ torr. However, the initial population of the Y-methylated intermediate I_y, accompanying formation of the corresponding C-methylated isomers I_α and I_β (eq 3a–c), cannot be directly

$$CH_3FCH_3^+ + \left[\underset{Y}{\langle \rangle} \right] \xrightarrow{-CH_3F}$$

$$\left[\underset{Y}{\overset{H}{\langle + \rangle}} \underset{CH_3}{\overset{H}{\smallsmile}} \right] [I]_\alpha \qquad (3a)$$

$$\left[\underset{Y}{\overset{H}{\langle + \rangle}} CH_3 \right] [I]_\beta \qquad (3b)$$

$$\left[\underset{\underset{CH_3}{|}}{\overset{+}{\langle \rangle}} \right] [I]_Y \qquad (3c)$$
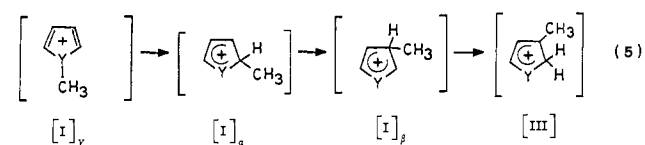
determined. In contrast with I_α and I_β, intermediate I_y cannot generate isolable methylated products without preliminary isomerization to a C-methylated intermediate, a route prevented under kinetically controlled conditions. Nevertheless, an estimate of the relative abundance of I_y, formed in the kinetically significant step of sequence 1a, can be inferred from a comparative analysis of Figures 5 and 6 for furan (3) and of the corresponding ones for thiophene (4) (Figures 9 and 10). In the case of furan, the 5:6 = 1.2 ratio, measured under kinetically controlled conditions (Figure 6), suddenly reaches its maximum apparent value of ca. 2.5 when the irradiation is carried out at 760 torr and without any added NMe_3. As the total pressure is lowered (Figure 5), this ratio slowly decreases to reach a value <1 at $P_{CH_3F} \leq 20$ torr. Qualitatively similar trends are observed for thiophene (Figures 9 and 10).

Such behavior can be explained by isomerization sequence 4,

$$I_y \xrightarrow{\text{fast}} I_\alpha \xrightarrow{\text{slow}} I_\beta \qquad (4)$$

whose first $I_y \rightarrow I_\alpha$ step proceeds nearly to completion, even at relatively high pressures (760 torr). The subsequent transfer $I_\alpha \rightarrow I_\beta$ appears to be inhibited by collisional quenching. It can be therefore concluded that the excited intermediates I tend to isomerize (eq 4) to the thermodynamically most stable isomer, which according to the experimental evidence, is a β-methylated intermediate, presumably with structure III (eq 5).[16]

$$\left[\underset{\underset{CH_3}{|}}{\overset{+}{\langle \rangle}} \right] \rightarrow \left[\underset{Y}{\overset{H}{\langle + \rangle}} \underset{CH_3}{\overset{H}{\smallsmile}} \right] \rightarrow \left[\underset{Y}{\overset{H}{\langle + \rangle}} CH_3 \right] \rightarrow \left[\underset{Y}{\overset{CH_3}{\langle + \rangle}} \underset{H}{\overset{CH_3}{\smallsmile}} \right] \quad (5)$$

$$[I]_Y \qquad [I]_\alpha \qquad [I]_\beta \qquad [III]$$

Figure 13. Positional selectivity of $CH_3FCH_3^+$ ions toward furan (3) and thiophene (4) and isomerization extent measured at P_{CH_3F} 20 torr.

Figure 14. Lower limits of the positional selectivity of $CH_3ClCH_3^+$ ions toward furan (3) and thiophene (4).

The relative abundance of the intermediates I_y from reaction 3c can be estimated from a comparison of the $\alpha:\beta$ isomeric distribution of the methylated products when the irradiation is carried out at 760 torr with or without added NMe_3 (Figures 6 and 10). In the absence of NMe_3, the $\alpha:\beta$ ratio increases to an extent that would reflect approximately the contribution by the fast $I_y \rightarrow I_\alpha$ step of sequence 4 to the population of the intermediates I_α and therefore the relative abundance of the corresponding species I_y. On this basis, we can evaluate the *intrinsic* positional selectivity of $CH_3FCH_3^+$ ions toward furan (3) and thiophene (4). The relevant figures are shown in Figure 13, together with the relative extent of the subsequent isomerization sequence 4, which occurs under thermodynamically controlled conditions.

Turning to the $CH_3ClCH_3^+$ attack on 3 and 4, the apparent contrast between the relatively poor reactivity of the methylating reactant and the high abundance of the (M + 15)+ and (M + 13)+ ions present in the CH_3Cl CI mass spectra of 3 and 4 suggests the predominant attack of the $CH_3ClCH_3^+$ ions on the n electrons of the heterocyclic compound with formation of the corresponding I_y intermediate. Such an hypothesis agrees well with the fact that, in the absence of NMe_3, i.e., when occurrence of isomerization sequence 5 is allowed, a significant increase of the relative yield of the α-methylated product is observed together with a simultaneous increase of the overall G_M value of the methylated products. However, the relatively limited yields of methylated products, recovered in the CH_3Cl sample without any added NMe_3, suggest that sequence 5 is not complete even at low pressures. Therefore, a significant fraction of the originally formed intermediates I_y might not have enough excitation energy to isomerize to one of the isomeric C-methylated species (I_α or I_β) before neutralization.[17] From these considerations, we conclude that a comparison of the $\alpha:\beta$ ratios, measured at 760 torr with or without NMe_3, can only provide an estimate of the *lower limit* of the $CH_3ClCH_3^+$ ion selectivity toward the heteroatom of 3 and 4 (Figure 14).

Isomerization sequence 5 can involve either an *intramolecular* methyl-group shift within the excited intermediates I (eq 6a)[18]

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(15) The radiolytic and CI experiments do not allow one to exclude that side processes 1b can involve also ionic species from the methylation-induced ring opening of the heterocyclic substrate.
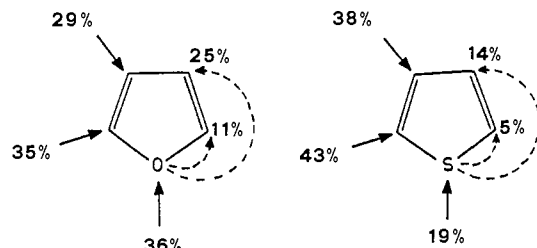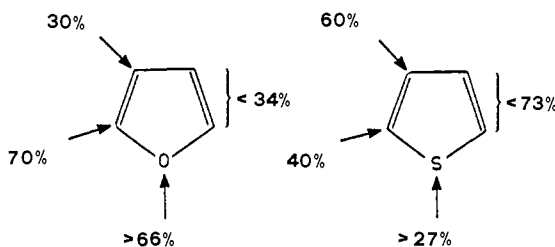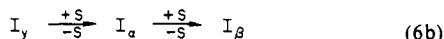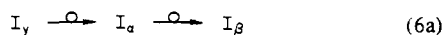
(16) Structure III for the thermodynamically most stable protonated β-methyl intermediates is assigned in conformity with the current view on substituent effects on heteroaromatic compounds (ref 2).

(17) It should be noted that $CH_3ClCH_3^+$ ion attack on 3 and 4 is ca. 10 kcal mol⁻¹ less exothermic than the corresponding methylation by $CH_3FCH_3^+$. The lower exothermicity of the $CH_3ClCH_3^+$ attack implies that the excitation level of intermediates (I) from $CH_3ClCH_3^+$ methylation of 3 and 4 can be appreciably lower than that of the same species from the $CH_3FCH_3^+$ attack.
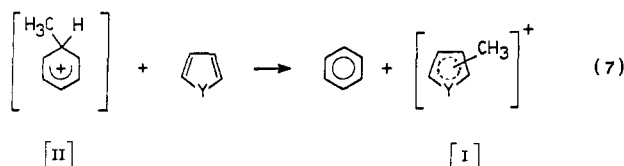
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or an *intermolecular* methyl-group transfer from I to another molecule of substrate (eq 6b). Although confirming the con-

$$I_\gamma \xrightarrow{-Q} I_\alpha \xrightarrow{-Q} I_\beta \qquad (6a)$$

$$I_\gamma \xrightarrow[-S]{+S} I_\alpha \xrightarrow[-S]{+S} I_\beta \qquad (6b)$$

S = heteroaromatic substrate

secutive character of the isomerization process (eq 5), the considerable increase of the β substitution observed at low pressure, preceded by accumulation of the α isomer at higher pressures (760 torr), does not provide any conclusive answer to this question. The only available evidence leading to the discrimination between the alternative sequences (6a and 6b) is provided by the dependence of the isomeric distribution of the methylated products upon the concentration of the heteroatomic substrate (Figure 15). The occurrence of the *intramolecular* isomerization mechanism 6a is supported by the constant α vs. β isomer distribution for a fourfold variation of the partial pressure of the heteroaromatic (P_S). In fact, these trends were all observed at atmospheric pressure and in the absence of NMe$_3$, i.e., under conditions allowing extensive $I_\gamma \rightarrow I_\alpha$ migration, while collisional deactivation makes the subsequent isomerization to I_β a comparatively slow process.

In the CH$_3$F competition experiments, the presence of benzene alters the isomeric distribution of the methylated heteroaromatic substrates. Thus a contribution of intermediate II to the formation of the methylated heteroaromatics can be inferred (eq 7). A
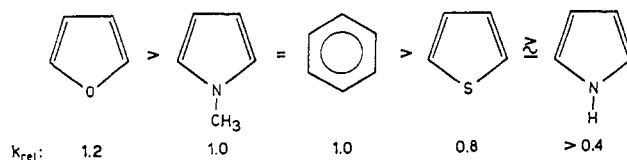
$$\left[\begin{array}{c} H_3C \; H \\ \times \\ \text{(+)} \end{array}\right] + \langle \text{pentagon} \rangle \longrightarrow \langle \text{hexagon} \rangle + \left[\langle \text{pentagon} \rangle^{CH_3} \right]^+ \qquad (7)$$

$$[\text{II}] \qquad\qquad\qquad\qquad [\text{I}]$$

preferential attack of II on the α position of 3 takes place. The β-carbons of thiophene (4) appear preferentially methylated by toluenium ion (II). These conclusions are substantiated by the dependence of the $\alpha{:}\beta$ isomer ratio of 5:6 and 7:8 on the relative concentration of the corresponding heterocyclic substrate vs. benzene ([S]/[B]) in the competition experiments (Figure 16), carried out at atmospheric pressure and in the absence of NMe$_3$. A significant increase of the α/β ratio from 3 is observed at low [S]/[B] ratios, i.e., under conditions favoring partial methylation of the heteroaromatic via process 7. An opposite trend can be inferred from the results of the 4/benzene competitions. At high NMe$_3$ concentrations (Figures 8 and 12), path 7 is blocked and a kinetic distribution of 5:6 and 7:8 is observed that is very close to that measured in the absence of benzene. Under thermodynamically controlled conditions (i.e., at pressure below 20 torr and in the absence of amine (Figures 7 and 11)), intramolecular isomerization sequence 5 shadows the effects of process 7. As a consequence, the relative yields of the β isomers 6 and 8 increase, to the extent that an α vs. β thermodynamic distribution is attained, which is similar to that measured in systems containing only the heteroaromatic substrate.

There is no apparent influence of benzene on the methylated heteroaromatics distribution from the CH$_3$Cl competition experiments. This suggests that occurrence of the intermolecular transfer 7 is much more limited than in the CH$_3$F systems. The scarce reactivity of the CH$_3$ClCH$_3^+$ toward benzene (and therefore the lack of significant concentrations of II) is likely responsible for such failure.

Substrate and Positional Selectivity. From the above results, which support the conclusions reached in the gas-phase methylation of pyrrole 1 and *N*-methylpyrrole (2),[1] we conclude that the kinetically most significant data are those measured at atmospheric pressure and in the presence of high concentrations of

NMe$_3$, i.e., under conditions where efficient collisional stabilization and rapid neutralization of intermediates I prevent occurrence of the secondary processes 1b and 1c. In such circumstances, product distribution is likely to reflect the original selectivity of the electrophile toward the selected substrates.

Prior to discussion of the *substrate* selectivity of CH$_3$FCH$_3^+$ ion toward furan (3) and thiophene (4), we must take into consideration that this is deduced from the apparent k_S/k_B ratios (=0.78 (3), 0.65 (4)) measured under *kinetically controlled conditions*. It follows that these ratios do not take into account the fraction of CH$_3$FCH$_3^+$ attack on the heteroatom of the substrate (36% (3), 19% (4)). The corresponding intermediates I_γ, in fact, cannot further evolve to neutral methylated products under kinetically controlled conditions. Correction of the apparent k_S/k_B ratios by a factor of 1.55 for 3 and 1.24 for 4 gives account of this fraction and provides the actual reactivity ratios ($k_{S'}/k_B$ = 1.2 (3), 0.8 (4)), on which to base any discussion on heteroaromatic reactivity. On these grounds, the following *intrinsic* heteroaromatic reactivity scale can be drawn:

The gas-phase reactivity order indicates that the CH$_3$FCH$_3^+$ ion attacks the selected aromatic substrates with approximately the same rate. The result is in good agreement with the remarkably low substrate selectivity of gaseous CH$_3$FCH$_3^+$ toward unencumbered aromatic substrates[6a,b] and with the available mass spectrometric data. In this case, it is found that, within the instrumental precision (ca. 20%), the rate constants of CH$_3$FCH$_3^+$ methylation of the selected heteroaromatics fall within the same order of magnitude.

In contrast with its lack of substrate discrimination, the CH$_3$FCH$_3^+$ ion exhibits a measurable, if modest, degree of *positional* selectivity toward furan 3 (Figure 13). The *intrinsic* directive properties of 3 toward gas-phase electrophilic CH$_3$FCH$_3^+$ methylation demonstrate the distinct tendency of furan to direct the electrophile predominantly toward the oxygen atom, i.e., the ring site with the maximum value of the net negative charge.[3a,b,4a,b] However, the rather indiscriminate attack of CH$_3$FCH$_3^+$ on the α- and β-carbons of 3 cannot be explained in terms of their individual charge density. In fact, Mulliken population analysis of the electronic charge distribution on furan invariably predicts the α-carbons to be positive while the β-carbons are usually found to have negative charge.[19]

The observed positional selectivity of furan toward CH$_3$FCH$_3^+$ is more consistent with the recent theoretical predictions based upon semiempirical calculations of the molecular electrostatic potentials determining the most attractive sites and pathways of attack on a furan molecule for an approaching charged electrophile.[5] In fact, analysis of the relevant equipotential energy contours for a ground-state furan molecule shows the presence of an intense attractive region around the oxygen atom. In addition, this attractive interaction may be instrumental in promoting α vs. β selectivity in the substrate, since vicinal α-carbons may interact by bending of the C$_\alpha$–H out of the plane of the molecule. In this view, *intrinsic* directive properties of furan toward a gaseous charged electrophile, such as CH$_3$FCH$_3^+$, can be considered as determined by the combined effects of the static electronic charge distribution of the substrate (which would favor electrophilic attack on the O and C$_\beta$ atoms) and the dynamical response of the electronic structure of the reactants in the heteroatom–electrophile interaction (which would increase the probability of α attack). In the case of CH$_3$FCH$_3^+$, the latter effect may be favored by

(18) The intramolecular methyl-group transfer within I is probably accompanied by fast proton shifts (cf. McLean C.; Mackor, E. L. *Discuss. Faraday Soc.* 1962, *34*, 165–176).

(19) (a) Hermann, R. B. *Int. J. Quantum Chem.* 1968, *2*, 165. (b) Preston, H. J. T.; Kaufman, J. J. *Int. J. Quantum Chem. Symp.* 1973, No. 7, 207–213. (c) Kaufman, J. J.; Preston, H. J. T.; Kerman, E.; Cusachs, L. C. *Ibid.* 1973, 249–260.
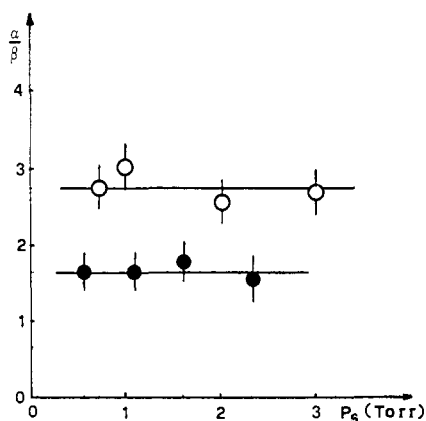
Electrophilic Methylation of Furan and Thiophene

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Figure 15. Dependence of the isomeric distribution of the methylated products ((O) methylfurans **5** and **6**; (●) methylthiophenes **7** and **8**) on the concentration of the heteroaromatic precursor (P_S) (P_{CH_3F} 760 torr).
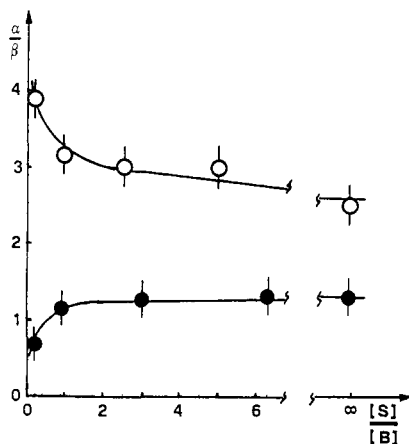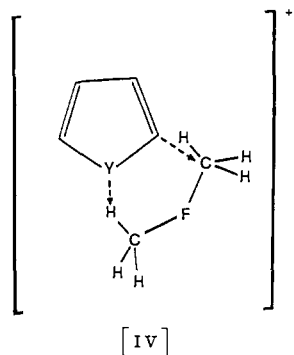

Figure 16. Dependence of the isomeric distribution of the methylated products ((O) methylfurans **5** and **6**; (●) methylthiophenes **7** and **8**) on the relative concentration of the corresponding heteroaromatic precursor vs. benzene ([S]/[B]) in the competition experiments (P_{CH_3F} 760 torr).

the recognized "chelating" properties of the electrophile, which would produce the electrostatic adduct IV by attack on the bi-

$$[IV]$$

dentate substrate (e.g., **3**).[6b,20] Of course, the significance of such adduct and, hence, of the relative extent of α substitution is determined by the intensity of the "hydrogen-bond-like" interaction between the hydrogens of the electrophile and the n electrons of the heteroatom. When this is negligible, as for pyrroles **1** and **2**, the positional selectivity of the substrate is essentially determined by its negative net charge distribution (N and C_β substitution).

When formation of the adduct IV is likely to occur, as for furan, α substitution is observed whose extent exceeds that predicted exclusively on the grounds of the electronic charge distribution in the substrate. In the case of thiophene, wherein any electrostatic interaction between the heteroatom and the electrophile is probably not significant,[21] the resulting positional selectivity is predominantly determined by the charge density of the reaction centers, i.e., $\alpha > \beta > S$.[22] Finally, an effective electrostatic interaction leading to an adduct similar to IV is not possible for the $CH_3ClCH_3^+$ ion. Most of the positive charge of this ion is located on the halogen atom. Therefore, $CH_3ClCH_3^+$ cannot efficiently "chelate" the heteroaromatic compound.[6a,b] Rather, a direct attack on the n center of the substrate predominantly takes place. The high stability of the resulting intermediate I_y confers to the heteroatom of **3** and **4** the role of $CH_3ClCH_3^+$ ion sink.

Conclusions

The present results provide conclusive support to the view that the gas-phase attack of $CH_3FCH_3^+$ ions on simple five-membered heteroaromatics is essentially regulated by the electrostatic interactions established within the encounter pair. In analogy with gas-phase aromatic substitutions by charged electrophiles, $CH_3FCH_3^+$ methylation of heteroaromatic compounds is characterized by a poor substrate discrimination, which sharply contrasts with a remarkable positional selectivity. Such a high selectivity is inferred from the kinetic predominance of the $CH_3FCH_3^+$ ion attack on those substrate position(s) with the highest negative net charge (C_β and N for pyrroles **1** and **2**, O for furan (**3**), and C_α for thiophene (**4**)). However, other factors play a role in determining site selection in simple heteroaromatics: (i) a repulsive electrostatic potential developed in the neighborhood of the N atom of **2** and (ii) an intense attractive potential region around the oxygen of furan, which increases the probability of substitution of the adjacent C_α positions. The latter effect applies in the case of bidentate electrophiles, such as the $CH_3FCH_3^+$ ion. Other electrophiles with different structural and electronic properties, such as the $CH_3ClCH_3^+$ ions, rather exhibit their inherent ability to condense selectively on the n-type nucleophilic center of the substrate.

The experimental trends reported in this study allow one to draw the following stability scale for the ionic intermediates originated from the methylation of simple heteroaromatics. The same order

$$[III] \qquad [V] \qquad [I]_y$$
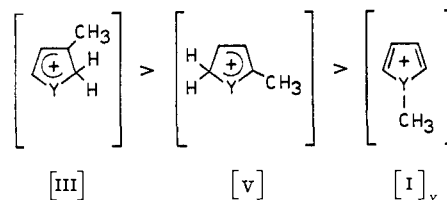
observed for **1** and **2** suggests that, within methylated heteroarenium intermediates, the stabilizing effect of the CH_3 group is maximum when the substituent and the heteroatom are located in the two positions adjacent to the protonated carbon (structure III).[23]

(20) See also: (a) Attinä, M.; Cacace, F.; Ciranni, G.; Giacomello, P. *J. Chem. Soc., Perkin Trans. 2* **1978**, 891–895. (b) Attinä, M.; Cacace, F.; Ciranni, G.; Giacomello, P. *J. Am. Chem. Soc.* **1977**, *99*, 5022–5026. (c) *Ibid.* 4101–4105. (d) Attinä, 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.

(21) Hydrogen bonds involving the "soft" sulfur atom are generally substantially weaker than the corresponding ones involving a "hard" oxygen atom. (Schuster, P.; Zundel, G.; Sandorfy, C. "The Hydrogen Bond"; North-Holland Publishing Co.: Amsterdam, 1976.) See also: (a) Desmueles, P. J.; Allen, L. C. *J. Chem. Phys.* **1980**, *72*, 4731–4748. (b) Kerns, R. C.; Allen, L. C. *J. Am. Chem. Soc.* **1978**, *100*, 6587–6594. (c) Purcell, K. F.; Drago, R. S. *Ibid.* **1967**, *89*, 2874–2879. (d) Vishnyakova, T. B.; Lobanov, V. V.; Pogorelyi, V. K. *Teor. Eksp. Khim.* **1980**, *16*, 534–539.

(22) (a) Gelius, V.; Roos, B.; Siegbahn, P. *Theor. Chim. Acta* **1972**, *27*, 171–185. (b) Bernardi, F.; Bottoni, A.; Mangini, A. *Gazz. Chim. Ital.* **1977**, *101*, 55–60.

(23) (a) Gilman, H.; Wright, G. *Chem. Rev.* **1932**, *11*, 323. (b) Gilman, H.; Butner, R. R. *J. Am. Chem. Soc.* **1933**, *55*, 2903. (c) Abraham, R. J.; Bullock, E.; Mitra, S. S. *Can. J. Chem.* **1959**, *37*, 1859–1869. (d) Chiang, Y.; Whipple, E. B. *J. Am. Chem. Soc.* **1963**, *85*, 2763–2767. (e) Whipple, E. B.; Chiang, Y.; Hinman, R. L. *Ibid.* 26–30. (f) Bean, G. P.; Wilkinson, T. J. *J. Chem. Soc., Perkin Trans. 2* **1978**, 72–77. (g) Alexander, R. S.; Butler, A. R. *Ibid.* **1980**, 110–112.

Time-Resolved Study of the Solvent and Temperature Dependence of Singlet Oxygen ($^1\Delta_g$) Reactivity toward Enol Ethers: Reactivity Parameters Typical of Rapid Reversible Exciplex Formation

A. A. Gorman,* I. R. Gould, and I. Hamblett

Contribution from the Chemistry Department, University of Manchester, Manchester M13 9PL, U.K. Received March 18, 1982

Abstract: Pulsed nitrogen laser excitation has been used to examine and compare the reactivities of four enol ethers toward singlet oxygen ($^1\Delta_g$) in five solvents. The experimental values of ΔH^* (0 ± 1.0 kcal mol^{-1}), ΔS^* (-23 to -34 eu), and the overall reaction rate constants (10^4–10^8 L mol^{-1} s^{-1}) are characteristic of excited-state processes involving rapid reversible exciplex formation. Solvent effects are small but in some cases significant. It is concluded that such effects are the result of solvation entropy requirements at the transition state leading from exciplex to product, particularly in the case of dioxetane formation. The possibility is raised that the reversible exciplex mechanism operates generally for O₂ ($^1\Delta_g$) reactions.

1. Introduction

The nature of the reaction of singlet oxygen, O₂ ($^1\Delta_g$), with alkenes and enol ethers to give "ene"-type products continues to be a subject of considerable discussion and argument.[1-6] The controversy has centered around two mechanisms involving (a) a classical six-center transition state and (b) a perepoxide intermediate. The advent of theoretical calculations in this area has in no way decreased mechanistic controversy. Orbital correlation diagrams[3] and CNDO/2 CI[7] and MINDO/3[8] calculations favour initial perepoxide formation. On the other hand GVB-CI[9] calculations are claimed to rule out this intermediate in favor of a 1,4 biradical although a concerted mechanism is not excluded.[10] More recently STO-3G and unrestricted MINDO/3 (UM3) results have been taken to exclude both perepoxide and biradical mechanisms and favor the concerted process.[12]

Experimentally it has been shown that for molecules containing a trisubstituted double bond, both enol ethers, and simple olefins, there exists a pronounced preference for hydrogen migration from the most substituted side of the double bond.[13] This, together

Scheme I

1
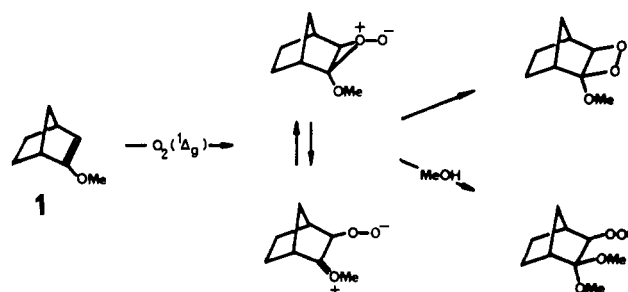
with small but apparently significant isotope effects,[11,14] led to the suggestion[15] that the initial reaction between O₂ ($^1\Delta_g$) and olefin is irreversible formation of a complex, the geometry of which, and subsequently that of the products, is determined by secondary orbital effects. It has, however, been argued that the steric preferences cited are consistent with ground-state conformational effects.[16]

Of particular interest have been reports of methanol trapping of intermediates.[17,18] In Scheme I are reproduced conclusions reached by Jefford and Rimbault[17] concerning the reaction of 2-methoxynorbornene (1) with O₂ ($^1\Delta_g$) in methanol. The isolation of the solvent addition product, shown not to be derived from the

(1) C. S. Foote, *Acc. Chem. Res.*, **1**, 104 (1968).
(2) K. Gollnick, *Adv. Photochem.*, **6**, 1 (1968).
(3) D. R. Kearns, *Chem. Rev.*, **71**, 395 (1971).
(4) K. Gollnick and H. J. Kuhn in ref 5, Chapter 8.
(5) "Singlet Oxygen", H. H. Wasserman and R. W. Murray, Ed., Academic Press, New York, 1979.
(6) A. A. Frimer, *Chem. Rev.*, **79**, 359 (1979).
(7) S. Inagaki and K. Fukui, *J. Am. Chem. Soc.*, **97**, 7480 (1975).
(8) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **97**, 3978 (1975); **99**, 2338 (1977).
(9) L. B. Harding and W. A. Goddard, *J. Am. Chem. Soc.*, **102**, 439 (1980).
(10) The biradical mechanism may be rejected on experimental grounds, particularly the proven suprafacial character of allylic hydroperoxide formation[11] and the lack of correlation of reactivity with radical stability.[1,3]
(11) M. Orfanopoulos and L. M. Stephenson, *J. Am. Chem. Soc.*, **102**, 1417 (1980).
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