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ORGANIC IONS IN THE GAS PHASE—XXI: SYNTHESIS AND MASS SPECTRA OF DEUTERIOTHIOPHENES

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Abstract—Mass-spectral and n.m.r. analysis of thiophenes labeled by exchange with deuteriosulfuric acid establishes that exchange at the 2 and 5 positions is essentially complete before any deuterium is incorporated at positions 3 and 4. Thus, such exchange is a satisfactory procedure for position-specific labeling. Mass spectra of the labeled thiophenes show that about 60% of the $[CHS]^+$ ion yield is derived from molecular ions that have not undergone prior rearrangement. The remaining 40% arises by a path or paths in which the four hydrogen atoms lose position identity. Other decomposition paths contributing to the mass spectrum are characterized by more nearly complete scrambling of hydrogens.

DURING studies of gas-phase reactions of aromatic compounds at high temperature and under electron-impact,[1-4] a need arose for thiophene-d_4. The attempted preparation by exchange with deuteriosulfuric acid in deuterium oxide, stirred at reflux for 16 hours, gave a product consisting chiefly of di- and monodeuteriothiophenes, with but little of the tri- and tetradeuteriated species. We had naively imagined that the reaction conditions were vigorous enough to attain nearly complete exchange. Evidently, the rate of exchange at the last two positions, presumably 3 and 4, was far lower than at the first two. This conclusion is in accord with reports,[5,6] which we had missed earlier, that the exchange rate with D_2SO_4 or the tritiated acid at positions 2 and 5 is about 1000 times as great as at positions 3 and 4.* More generally, molecular-orbital calculations and considerable experimental data indicate that the 2 and 5 positions are substantially more reactive than the 3 and 4 in nucleophilic, free-radical, and electrophilic substitution reactions.[7] An attempt to account for a parallel difference in reactivity in platinum-catalyzed deuteriation of thiophene led to a rather detailed mechanistic proposal for the interaction between the molecule and the catalyst surface.[8] The far smaller reactivity difference with platinum[8] than with the acid would seem, in retrospect, more in need of a special rationale.

In view of these preliminary results, we extended the reaction time ultimately to 1212 hours, adding fresh D_2SO_4 at intervals. The isotopic compositions of the thiophene samples so obtained cover a sufficiently wide range to permit derivation from their mass spectra of the spectra corresponding to each of the pure isotopic species. Such calculation is based on the assumption that the number of deuterium atoms in the thiophene molecule defines the chemical species: that is, that the isomer distribution of thiophene-d_2, for example, is the same in all the samples in which it

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* Although these kinetic studies[5,6] established a large difference between the exchange rates at the two positions, the composition of the labeled thiophenes, in the absence of n.m.r. and mass spectral analysis, is not entirely clear.

occurs; or, if the isomer distribution varies, that the spectra of the isomers are identical. We assumed tentatively that the d_1, d_2 and d_3 species in these products comprised chiefly thiophenes-2-d, -2,5-d_2 and -2,3,5-d_3. To supplement these results and to check on the validity of the assumption, we also prepared thiophenes-2-d and -2,5-d_2 by specific labeling procedures and measured their mass spectra.

Previous work on the mass spectra of thiophene and derivatives shows extensive loss of position identity of atoms in decomposition under electron-impact.[4,9to15] The spectra clearly contain, however, some contributions from processes not preceded or accompanied by reorganization of the molecular ion. In most cases, the ions so formed are accompanied by ions having the same elemental composition but arising by other paths, so that the relationships between the original molecular structure and the spectrum are somewhat obscured. In particular, D. H. Williams *et al.*[14] reported, while the present paper was in preparation, that $[CHS]^+$ formation from thiophene is preceded by partial randomization of hydrogen atoms and that the relative contribution arising with randomization increases as ionizing voltage is reduced. The only other process that they examined, loss of C_2H_2 from the molecular ion, is preceded or accompanied by loss of position identity of the four hydrogen atoms.

RESULTS

Exchange with D_2SO_4

To better define the discontinuity following exchange of the first two atoms with D_2SO_4, we calculated the atom % deuterium in each of the products listed in Table 1 and, by the usual procedure employing the binomial coefficients, the corresponding

Table 1. Deuteriation by exchange with D_2SO_4

Reaction time, hrs.	Number of 50 g portions of 50% D_2SO_4	Isotopic composition, %				
		d_0	d_1	d_2	d_3	d_4
16	1	3·4	29·7	64·5	2·3	0·1
38	2	0·7	14·8	76·2	8·1	0·2
102	4	0·0	3·8	57·0	33·6	5·6
438	5	0·0	1·3	21·2	47·9	29·6
1212	6	0·0	0·6	7·0	34·2	58·2

Table 2. Spectra of the isotopically pure thiophenes
Relative intensity*†‡

m/e	d_0	d_1	d_2§	d_2‖	d_3	d_4
25	0·79	0·58	0·35	0·35	0·27	−0·10
26	1·99	1·30	0·67	0·69	1·03	0·78
27	0·45	1·27	1·89	1·93	1·42	−0·25
28	0·06	0·34	0·44	0·41	1·69	2·72
29	0·01	0·01	0·17	0·18	0·43	0·00
30	0·00	0·00	0·01	0·00	0·15	0·42
32	1·43	1·53	1·54	1·52	1·94	1·34
33	0·32	0·22	0·14	0·12	0·11	−0·01
34	0·13	0·18	0·26	0·24	0·34	0·30
36	0·48	0·46	0·44	0·43	0·47	0·33
37	2·19	1·47	0·87	0·86	0·47	−0·11
38	2·39	1·82	1·48	1·53	1·82	1·66

TABLE 2. (*continued*)

m/e	d_0	d_1	d_2§	d_2‖	d_3	d_4
39	7·39	3·38	1·59	1·61	1·23	−0·12
40	0·41	5·31	4·49	4·60	1·44	2·18
40·5	0·22	0·13	0·07	0·07	0·08	−0·04
41	0·43	0·42	3·02	3·08	5·37	−0·18
41·5	0·04	0·22	0·24	0·24	0·16	−0·01
42	0·90	0·04	0·28	0·36	1·47	7·64
42·5	0·04	0·91	0·02	0·01	0·02	0·03
43	0·04	0·06	0·95	0·96	−0·03	0·31
43·5	0·00	0·04	0·05	0·06	0·87	0·00
44	0·78	0·75	0·72	0·72	0·66	1·38
45	15·10	9·48	3·85	3·94	1·71	0·83
46	0·39	6·33	12·10	11·94	13·67	14·89
47	0·67	0·57	0·43	0·44	0·55	0·18
48	0·25	0·46	0·71	0·71	0·82	0·77
49	1·06	0·68	0·34	0·32	0·37	−0·18
50	2·03	1·24	0·93	0·92	0·98	0·40
51	1·14	1·59	1·41	1·34	0·85	−0·05
52	0·06	0·95	1·19	1·19	1·63	1·74
53	0·00	0·06	0·72	0·70	0·87	−0·03
54	0·00	0·01	0·05	0·06	0·45	1·07
55	0·00	0·01	0·02	0·02	0·11	−0·03
56	0·52	0·48	0·41	0·40	0·50	0·29
57	4·15	2·92	1·69	1·68	1·03	−0·21
58	17·83	9·99	4·42	4·37	3·39	3·89
59	0·72	9·21	13·45	13·39	8·63	−0·05
60	0·79	0·71	2·75	2·82	8·47	19·37
61	0·02	0·41	0·67	0·65	0·65	0·55
62	0·00	0·01	0·10	0·11	0·42	0·79
68	0·21	0·19	0·11	0·16	0·19	0·09
69	2·04	1·45	0·87	0·86	0·42	−0·05
70	0·09	0·60	1·03	1·04	1·13	1·85
71	0·09	0·10	0·06	0·09	0·10	0·03
72	0·00	0·03	0·05	0·05	0·10	0·03
80	0·17	0·14	0·12	0·10	0·13	0·01
81	1·08	0·62	0·27	0·31	0·13	−0·01
82	0·76	0·64	0·63	0·61	0·61	0·51
83	1·63	0·70	0·45	0·44	0·24	−0·01
84	25·91	1·17	0·73	0·70	0·40	0·37
85	1·40	25·70	0·70	0·65	0·85	−0·12
86	1·17	1·41	27·02	26·77	0·42	0·85
87	0·05	1·18	1·45	1·41	25·21	0·05
88	0·01	0·05	1·22	1·30	1·27	29·24
89	0·00	0·01	0·07	0·06	1·10	1·55
90	0·00	0·00	0·01	0·00	0·11	1·25

* Expressed as per cent of total-ion intensity from *m/e* 25 to 91.

† Intensities have been omitted from the table at masses where all six values are lower than 0·10.

‡ Not corrected for naturally occurring heavy-isotopic contributions.

§ Derived from the spectrum of the specifically labeled thiophene-2,5-d_2.

‖ Derived from the spectrum of the labeled thiophene prepared by exchange with D_2SO_4 with a reaction time of 38 hours.

statistical compositions. These are listed in Table 3. Comparison of the observed and statistical compositions shows good agreement only in the 1212-hour product.

TABLE 3. CALCULATED STATISTICAL ISOTOPIC COMPOSITIONS

Reaction time, hrs	Atom % deuterium*	d_0	d_1	d_2	d_3	d_4
16	41·5	11·7	33·2	35·4	16·7	3·0
38	48·0	7·3	27·0	37·4	23·0	5·3
102	60·3	2·5	15·1	34·4	34·8	13·2
438	76·5	0·3	4·0	19·4	42·1	34·2
1212	87·5	0·0	0·7	7·2	33·5	58·6

* Derived from the isotopic analyses in Table 1.

As an alternative way of viewing the data, we calculated a constant k defined as the $d_3:d_2$ concentration ratio. Table 4 lists, for each of the five exchange products, k_1, the observed ratio; k_2, the ratio derived from the statistical compositions shown in Table 3; and k_1/k_2. The value of k_1/k_2 rises with reaction time and reaches unity in the 438-hour product, even though the overall isotopic composition in that product still differs considerably from statistical. By way of comparison, the isotopic distribution of thiophenes recovered from platinum-catalyzed deuteration[8] yields values of k_1, k_2 and k_1/k_2, respectively, of 0·163, 0·278 and 0·586. The last of these is about the same as that obtained by refluxing with D_2SO_4 only after 102 hours.

TABLE 4. $d_3:d_2$ CONCENTRATION RATIOS

Reaction time, hrs	k_1, from values in Table 1	k_2, from values in Table 3	k_1/k_2
16	0·0357	0·472	0·076
38	0·106	0·615	0·172
102	0·589	1·012	0·581
438	2·26	2·17	1·04
1212	4·89	4·65	1·05

Decomposition processes

Five decomposition reactions can be inferred from the spectra:

$[C_4H_4S]^+ \rightarrow [C_4H_3S]^+ + H$ 1
$[C_4H_4S]^+ \rightarrow [C_3HS]^+ + CH_3$ 2
$[C_4H_4S]^+ \rightarrow [C_2H_2S]^+ + C_2H_2$ 3
$[C_4H_4S]^+ \rightarrow [CHS]^+ + C_3H_3$ 4
$[C_4H_4S]^+ \rightarrow [C_3H_3]^+ + CHS$ 5

Intensities in the mass regions corresponding to the product ions, corrected for naturally occurring heavy isotopic contributions, are shown in Table 5. At this stage of the work, the negative intensity values in Table 2 were replaced by zeroes. The monoisotopic intensities were used to estimate label retentions[16] in the fragment ions in the spectrum of each labeled thiophene.

TABLE 5. MONOISOTOPIC INTENSITIES, SELECTED MASS REGIONS

m/e	Ion*	d_0	d_1	d_2†	d_2‡	d_3	d_4
39	$[C_3H_3]^+$	7·31	3·32	1·54	1·56	1·17	0·00
40		0·17	5·20	4·44	4·53	1·38	2·18
41		0·42	0·25	2·87	2·92	5·21	0·00
42						1·30	7·64
45	$[CHS]^+$	15·10	9·48	3·85	3·94	1·71	0·83§
46		0·10	6·15	12·03	11·87	13·64	14·87
56		0·52	0·48	0·41	0·40	0·50	0·29
57		4·13	2·91	1·68	1·67	1·01	0·00
58	$[C_2H_2S]^+$	17·68	9·88	4·35	4·30	3·34	3·88
59		—	8·78	13·24	13·19	8·48	0·00
60		—	—	2·16	2·23	8·07	19·20
68		0·21	0·19	0·11	0·16	0·19	0·09
69	$[C_3HS]^+$	2·03	1·44	0·87	0·85	0·41	0·00
70		—	0·53	0·99	1·00	1·10	1·71
80		0·17	0·14	0·12	0·10	0·13	0·01
81		1·07	0·61	0·26	0·30	0·12	0·00
82		0·70	0·60	0·61	0·59	0·60	0·51
83	$[C_4H_3S]^+$	1·54	0·64	0·41	0·39	0·21	0·00
84	$[C_4H_4S]^+$	25·80	1·11	0·68	0·65	0·39	0·35
85		—	25·61	0·65	0·60	0·82	0·00
86		—	—	26·95	26·71	0·36	0·83
87		—	—	—	—	25·15	0·01
88		—	—	—	—	—	29·20

* Formulae are shown opposite masses of the corresponding unlabeled ions only.

† See footnote §, Table 2.

‡ See footnote ||, Table 2.

§ Origin of this peak is not clear. It would seem to be in error.

1. $[C_4H_4S]^+ \rightarrow [C_4H_3S]^+ + H$. Intensities in the molecular region indicate that (a) the overall probability of losing one or more hydrogen atoms but no carbons tends to decrease with increasing deuterium content; (b) the probability of losing a protium atom (as measured by intensity at the molecular mass less 1) is approximately proportional to the number of protium atoms in the molecule; and (c) the probability of losing deuterium from thiophene-d_4 (as measured by intensity at the molecular mass less 2) is 54% that of losing protium from the unlabeled compound. In regard to point (b), the discrepancies from random statistics in the loss of protium presumably stem from isotope effects. The direction of the discrepancies is opposite to that expected from a conceivable contributing process by which hydrogen would be lost specifically from positions 3 and 4, analogous to the reported[10] preferential loss from position 3 in benzothiophene. Preferential loss from positions 2 and 5 might be involved.

2. $[C_4H_4S]^+ \rightarrow [C_3HS]^+ + CH_3$. Intensities in the mass-69 region indicate that (a) the overall probability of this process tends to decrease with increasing deuterium content of the thiophene, except possibly in going from d_3 to d_4; and (b) distribution of the protium and deuterium atoms between the products (estimated from intensities at 69 and 70) is almost exactly statistical. The observed and statistical retentions, respectively, for the partially deuteriated thiophenes are: d_1–27%, 25%; d_2–53 and 54%, 50%; and d_3–73%, 75%.

3. $[C_4H_4S]^+ \rightarrow [C_2H_2S]^+ + C_2H_2$. Observed and statistical retentions, respectively, in the $[C_2H_2S]^+$ ions (one deuterium atom in the thiophene-d_1 spectrum, two in the others) are: d_1–50%, 50%; d_2–12 and 13%, 17%; and d_3–46%, 50%. As found also by Williams,[14] the agreement is good. The discrepancies are appreciable, however, and suggest a reluctance to retain the atoms at both positions 2 and 5. The mechanistic significance of these discrepancies is not clear.

4. $[C_4H_4S]^+ \rightarrow [CHS]^+ + C_3H_3$. Intensities at masses 45 and 46 imply partial randomization, as was observed also by Williams.[14] The retention values–37·8% in d_1, 75·8 and 75·0% in d_2 (Williams found 78%[14]) and 88·9% in d_3—are intermediate between the values to be expected for a process **4a** in which $[HCS]^+$ is formed with no prior scrambling of atoms and contains hydrogen derived solely from position 2 or 5, and a process **4b** in which the four thiophene hydrogens contribute statistically in forming the $[HCS]^+$ ion. If $[HCS]^+$ is assumed to arise by these two processes, their relative contributions can be calculated from the observed retentions. The values so found for the contribution of **4a** are: d_1, 51·2%; d_2, 51·6 and 50·0%; d_3, 55·6%; average, 52% ± 2% (average deviation). As has been suggested,[14] process **4b** may well resemble the photochemically induced skeletal rearrangement that has been demonstrated to occur in substituted thiophenes.[17]

The relative contributions of the two processes permit an independent check on the assumption that the exchange-deuteriated thiophene-d_3 consists almost solely of the 2,3,5-d_3 isomer. Taking these contributions as 52 and 48%, the calculated label retentions in $[CHS]^+$ derived respectively from 100% 2,3,5-d_3, 100% 2,3,4-d_3 and 90% 2,3,5-d_3 plus 10% 2,3,4-d_3 thiophenes are 88·0%, 62·0% and 85·4%. The 2,3,4-d_3 isomer would appear thus to comprise less than 10% of the thiophene-d_3, probably by a substantial margin.

5. $[C_4H_4S]^+ \rightarrow [C_3H_3]^+ + CHS$. Because of possible interference from labeled $[C_3H_2]^+$ ions, total $[C_3H_3]^+$ intensities in the thiophene-d_1 and -d_2 spectra were assumed equal to that in the d_0 spectrum, where it appears solely at mass 39. In the d_3 spectrum, such interference is not possible, and the sum of intensities at masses 41 and 42 was taken as the measure of total $[C_3H_3]^+$ yield. Observed and statistical retentions in the $[C_3H_3]^+$ ions (one deuterium atom in the thiophene-d_1 spectrum, two in the d_2, and three in the d_3) are: d_1–71·1%, 75%; d_2–39·2 and 40·0%, 50%; and d_3–20·0%, 25%. The discrepancies are appreciable and all in the same direction, and thus could be accounted for by two contributing processes, **5a** and **5b**, complementary to **4a** and **4b**, that is, defined in the same way as **4a** and **4b** but with the charge now going to the C_3H_3 particle rather than to the CHS. By the analogous calculation, the values found for the contribution of **5a** are: d_1, 15·6%; d_2, 21·6 and 20·0%; d_3, 20·0%; average, 19% ± 2% (average deviation). Almost twice as large a fraction of the total $[C_3H_3]^+$ yield as of the neutral C_3H_3 apparently arises by a path in which the four thiophene hydrogens are scrambled.

CONCLUSION

The cumulative n.m.r. and mass-spectral evidence, in good accord with previous studies of exchange with D_2SO_4,[5] indicates that exchange at positions 2 and 5 is essentially complete before a third deuterium atom enters the molecule. This deuteriation procedure thus yields thiophene labeled in high positional specificity.

Decomposition of thiophene under electron-impact differs sharply from that of benzene in that substantial amounts of products from the former are apparently derived from molecular ions with the original thiophene structure, or possibly with the ring opened but with no hydrogen scrambling. In benzene, in contrast, all the known primary decomposition products arise by processes in which the six hydrogen atoms completely lose position identity.[18,*] Any attempt to rationalize the differing behavior must focus on the role of the sulfur atom, which, in introducing asymmetry into the ring, may serve as a center for chemical reactivity and perhaps for charge localization.

EXPERIMENTAL

Materials. A mixture of 15·73 ml (0·2 mole) of unlabeled thiophene (API standard sample) and 50 g of 50% D_2SO_4 in D_2O (0·5 mole D_2SO_4, 1·25 mole D_2O) was stirred at reflux. The cooled thiophene layer was separated and stirred at reflux with a fresh portion of 50% D_2SO_4 in D_2O. The number of such portions of D_2SO_4, total reaction time and isotopic composition of the recovered thiophene (80 to 85% recovery) are shown in Table 1.

Thiophene-2-*d* was obtained in 51% yield by hydrolysis with 10% D_2SO_4 in D_2O of the Grignard reagent from 32·6 g (0·2 mole) of 2-bromothiophene and 5·28 g (0·22 g-at) of magnesium. It had the isotopic composition 1·4% d_0, 96·7% d_1, and 1·9% d_2.

Thiophene-2,5-d_2 was prepared by Bak's procedure.[19] A mixture of 48·39 g (0·2 mole) of 2,5-dibromothiophene, 27·52 g (0·4 g-at) of zinc dust, 100 ml (5 moles) of D_2O and 18·84 ml (0·2 mole) of acetic anhydride was stirred at reflux for 60 hours, then distilled. The thiophene was dried over Drierite and redistilled to yield 11·9 g (70%) of thiophene-2,5-d_2, boiling at 82°. The isotopic composition was 0·1% d_0, 4·8% d_1, 94·8% d_2, and 0·3% d_3.

The specificity of deuterium incorporation in the thiophenes-2-*d* and -2,5-d_2 was confirmed by n.m.r., which showed that the 38-hour exchange product had 12% of the protons in positions 2 and 5, and 88% in positions 3 and 4; estimated uncertainty was $\pm 2\%$. The corresponding values derived from the mass-spectral isotopic analysis (Table 1) are 8% and 92%, on the assumption that positions 2 and 5 are labeled in all cases before a third deuterium is introduced. Agreement with the n.m.r. data is good, supporting the validity of the assumption.

Mass spectrometry. Mass spectra were measured on a modified[20] Consolidated model 21-103 instrument at an electron energy of 70 volts, with the source and inlet system both at 250°. Isotopic compositions were derived from low-voltage measurements,[21] ignoring possible isotope effects on sensitivity.[22] For the low-voltage measurements, the repellers were set at an average potential of 3 volts, the exact values—4·00 volts on the inner repeller and 2·00 on the outer one—being selected to give maximum sensitivity.

Table 2 shows the spectra of the isotopically pure species derived from the experimental spectra on the assumption that the number of deuterium atoms is sufficient to define the chemical species. Successive subtractions of one experimental or derived spectrum, multiplied throughout by an appropriate factor, from another were monitored by keeping track of the isotopic composition. In this derivation, we used the spectra of the unlabeled compound, the two specifically labeled ones, and the 438-hour and 1212-hour exchange products. A second spectrum of thiophene-d_2 was calculated by using the spectra so derived for all species other than d_2 to remove the isotopic impurities from the 38-hour exchange product. The two thiophene-d_2 spectra are virtually identical, further supporting the assumption underlying the calculations. Negative intensity values in the derived spectra probably stem chiefly from failure of this assumption to hold rigorously. Their small number and low values, however, suggest that the resultant errors are slight.

In accord with Williams' observations,[14] our spectra show metastable peaks corresponding to the loss of C_2H_2 from the unlabeled molecule, C_2H_2 and C_2HD from the d_1, C_2HD from the d_2, C_2HD and C_2D_2 from the d_3, and C_2D_2 from the d_4.

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