of pure **1** and of a sample of **1** collected after 39 hr were the same within experimental error. Similarly, nmr and infrared spectra of material from this peak, isolated even after 32 days in the acid solutions, were identical with those of pure **1**. On standing in aqueous acid, **1** was converted ultimately to a complex mixture of compounds, some of which separated from the aqueous solution. The concentration of **1** remaining could be estimated using its characteristic nmr absorptions (particularly the complex absorptions of the cyclopropyl hydrogens). In several experiments it was noted that the rate of disappearance of **1** had a half-time of greater than 1 month.

The sample to be analyzed was transferred to the mass spectrometer. The height of the 73 relative to the 71 peak and of the 47 relative to the 45 peak was determined carefully with a slow sweep. For every sample, to eliminate small errors due to drifting with time, a given peak (n) was swept 4–12 times, the accompanying peak ($n + 2$) swept a corresponding number of times, and the original peak again swept the same number of times. All values were averaged to obtain the relative heights of the peaks. Ratios determined on the same day were generally reproducible to 0.0005 in the range (0 to 0.1) in which the ratios fell.

The pseudo-first-order rate constants for exchange then were calculated from the usual first-order rate expression for an exchange process.[20] The concentrations of O^{18}-labeled **1** to put into this expression were taken from values of (height$_n$)/(height$_n$ + height$_{n+2}$) for the labeled samples from which were subtracted the (small) value of this term obtained for unlabeled **1**.[21] For each run (two runs with 6 and 8 significant points, respectively), separate rate constants were determined with a least-squares computer program using the data from the two sets of mass spectral peaks.

A similar experiment used D_2O instead of H_2O^{18} as the solvent. After 22 hr, the solution (10 ml) was poured into 10 ml of ether. The ether solution was washed with four 5-ml portions of 0.01 M aqueous perchloric acid and with 5 ml of a concentrated potassium carbonate solution, dried over Drierite, and concentrated. The **1** isolated by chromatography gave 72:71 and 46:45 ratios the same within experimental error as those given by pure **1** and exhibited an infrared spectrum identical with that of pure **1**.

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Organic Ions in the Gas Phase. XVIII. Mass Spectra of Nitroarenes

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Contribution from the Research and Development Department, American Oil Company, Whiting, Indiana, and Research Department, Amoco Chemicals Corporation, Whiting, Indiana. Received April 30, 1966

Abstract: The mass spectra of unlabeled and deuterated isomeric nitrotoluenes, of the isomeric nitrobiphenyls, and of a dimethoxy-2-nitrophenol help define the roles of steric and mesomeric effects in decomposition of nitroarenes under electron impact. Intramolecular oxidation–reductions and isomerization to aryl nitrites, prominent in these systems, parallel and can thus serve as precedents for interpretation of thermal and photochemical reactions.

An exploratory study of aromatic nitration[2] furnished an opportunity and incentive to study the mass spectra of a group of nitroarenes. The most prominent features of nitroarene spectra are well known.[3–12] Nitrobenzene and many derivatives show evidence for primary loss of O, NO, and NO_2,[13] and for formation of NO^+. Derivatives with an *ortho* substituent containing α hydrogens—CH_3, NH_2, or OH—show primary loss of OH rather than O; such loss of OH is often followed by loss of CO. Mechanistic details of this reaction sequence, as well as of competing processes, have been the subject of study and speculation.

The pronounced effects of *ortho* substitution on the mass spectra of nitroarenes are presumably related to the wide range of poorly understood reactions displayed by *ortho*-substituted nitroarenes in more conventional chemical[14] and photochemical[15] systems. Within the

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(1) (a) American Oil Co.; (b) Amoco Chemicals Corp.

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narrower bounds of mass spectra alone, the characteristic loss of OH from *ortho*-substituted nitroarenes apparently fits into a common pattern with reactions observed in ionic decomposition of other classes of *ortho*-substituted aryl compounds: acids and esters,[16,17] benzyl alcohols,[18] sulfones,[19] diarylmethanes,[20] and diaryl ethers.[21] The hope of confirming "obvious" aspects of this reaction and perhaps clarifying subsequent reaction steps prompted us to examine spectra of deuterium-labeled *o*-, *m*-, and *p*-nitrotoluenes.

A recent paper[10] observes that "the isomeric nitroanilines [paralleled closely by the nitrophenols] show features in common with the nitrotoluenes but the differences between spectra are less marked." However, subsequent discussion and spectral data in the same paper suggest that a better statement might have been that the differences between *ortho* and non-*ortho* isomers are less marked, but that those between the *meta* and *para* isomers are greater than between the corresponding nitrotoluenes. The pronounced differences between spectra of *meta* and *para* isomers of at least some nitrobenzene derivatives contrast sharply with the close similarity usually exhibited by spectra of the corresponding position isomers of dialkylbenzenes.[22] The differing behavior of the two classes of compounds is presumably related to differing charge distributions in the ionized molecules and in decomposition products derived from them. We have supplemented the published spectra with those of the three isomeric nitrobiphenyls and 4,5-dimethoxy-2-nitrophenol, selected as model compounds to assist correlation of selected spectral features with electron-releasing or -withdrawing properties of functional groups.[11,23]

Experimental Section

We have measured the spectra of *o*- and *p*-nitrotoluenes unlabeled and -*α*-*d*; *m*-nitrotoluene unlabeled and -2,4,5,6-d_4; *o*-, *m*-, and *p*-nitrobiphenyls; and 4,5-dimethoxy-2-nitrophenol. The samples of the three unlabeled nitrotoluenes and *m*-nitrotoluene-d_4 were kindly supplied by L. C. Leitch, of the National Research Council of Canada; that of 4,5-dimethoxy-2-nitrophenol was a gift from A. Taurins, of McGill University. The nitrobiphenyls were purchased from the Aldrich Chemical Co.

The labeled *o*- and *p*-nitrotoluenes were prepared by nitrating toluene-*α*-*d* from hydrolysis of benzylmagnesium bromide in deuterium oxide.[24] A mixture of 0.77 g of 90% nitric acid and 1.50 g of 96% sulfuric acid was added dropwise through a capillary to 1.0 g of toluene-*α*-*d* with stirring at 10°. After being stirred for 2 hr, the reaction mixture was poured on ice and extracted with ether. The organic layer was washed with sodium bicarbonate solution, then with distilled water, and dried over sodium sulfate. Removal of the ether left an isomeric mixture of nitrotoluenes-*α*-*d* which were separated by preparative gas chromatography.

Spectra were measured with 70-v electrons on a modified[25] Consolidated Model 21-103 instrument with the inlet system at 250°. Isotopic composition (see Table I) of labeled materials was estimated from low-voltage measurements.[26] Selected portions of the spectra of the *o*-nitrotoluenes were scanned over a range of reduced ionizing voltages to see whether label retention in fragment ions varies with voltage. For all low-voltage work, repellers were maintained at an average potential of 3 v; actual settings, adjusted for maximum ion current, were 3.60 v on the inner repeller and 2.40 v on the outer one.

Table I

	Un-labeled, %	Deuterium, %			
		d_1	d_2	d_3	d_4
o-Nitrotoluene-*α*-*d*	4.1	95.9	...	...	...
p-Nitrotoluene-*α*-*d*	4.1	95.9	...	...	...
m-Nitrotoluene-2,4,5,6-d_4	0.3	...	0.1	4.4	95.2

Partial spectra of the nitrotoluenes, the nitrobiphenyls, and the dimethoxynitrophenol are shown in Tables II, III, and IV, respectively, with relative intensities expressed on a scale on which total intensity at *m/e* 25 and above equals 100.0. No corrections have been made for naturally occurring heavy isotopic species because the exact elemental compositions of ions at many masses are uncertain; isobaric species are not resolvable with our instrument. Where such corrections were required to estimate label retentions in fragment ions,[22] we used approximate calculations, which appear adequate for the purpose. Contributions of isotopic impurities have been removed form the spectra of the labeled *o*- and *p*-nitrotoluenes, but not from that of the *meta* isomer.

Discussion

Nitrotoluenes. *ortho vs. meta–para* **Substitution.** In the spectrum of *o*-nitrotoluene, intensities at the parent mass less 17, less 44, less 45, and less 47 units are higher, and those at the parent mass and the parent mass less 16, less 30, less 46, and less 58 are lower than in those of the *meta* and *para* isomers. These contrasting patterns as well as metastable peaks[27] point to gross differences in the underlying chemistry. The most abundant primary reaction product in the spectrum of *o*-nitrotoluene arises by loss of OH, which may be followed by loss of either CO or HCN; competition from this group of reactions evidently reduces the yields of products from primary loss of O, NO, and NO_2. The ion of parent mass less 58, included in the latter group, apparently arises by sequential loss of NO and CO. The spectra of the *meta* and *para* isomers show essentially nothing corresponding to primary loss of OH and associated secondary reactions. The difference in intensity at the parent mass less 47 units, coupled with appreciable intensities at this mass in all three spectra, suggests that this peak includes contributions from two separate processes: in one, the elements of HNO_2 are lost as a unit or possibly as NO_2 and H; in the other, they are lost in two steps, as OH and NO. These reactions are summarized in Chart I, in which solid arrows are used for processes supported by metastable peaks.

The above observations constitute strong circumstantial evidence that the hydrogen atom lost as OH from the *ortho* isomer comes from the methyl group,

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(27) Reference 10 reports several metastable peaks in the spectra of the nitrotoluenes in addition to those observed by us.

Table II. Partial Spectra of Nitrotoluenes

		Relative intensity					
		ortho		*meta*		*para*	
Mass	Ion[a]	Unlabeled	α-d[b]	Unlabeled	2,4,5,6-d_4[c]	Unlabeled	α-d[b]
142		...	...	...	1.01	...	...
141		...	...	...	10.8	...	...
140		...	0.02	...	0.73	0.01	0.09
139		0.02	0.20	0.09	0.06	0.08	1.04
138		0.18	2.40	1.00	...	1.03	12.7
137	$C_7H_7NO_2^+$	2.18	...	12.1	...	12.5	...
126		...	...	...	0.05	...	...
125		...	...	...	0.56	...	...
124		...	0.01	...	0.07	...	...
123		0.02	0.06	0.01	0.08	0.01	0.03
122		0.07	0.94	0.05	0.01	0.03	0.33
121	$C_7H_7NO^+$	1.14	10.5	0.58	0.01	0.35	0.03
120	$C_7H_6NO^+$	12.9	2.44	0.08	0.01	0.03	0.02
119		0.06	0.02	0.04	0.01	0.01	0.02
112		...	...	...	0.15	...	...
111		...	...	...	1.66	...	...
110		...	...	...	0.19	...	0.02
109		0.01	0.06	0.01	0.11	0.02	0.38
108		0.06	0.39	0.14	0.08	0.38	4.81
107	$C_7H_7O^+$	0.41	0.14	1.88	0.06	4.83	0.09
97		...	...	...	0.08	...	...
96		...	...	...	2.07	...	...
95		...	0.05	0.01	26.4	...	0.01
94		0.06	0.70	...	2.34	0.01	0.06
93	$C_6H_5O^+$	1.05	6.70	0.07	1.57	0.06	1.66
92	$C_6H_6N^+$	8.99	14.4	2.07	1.56	1.63	21.2
91	$C_7H_7^+$	11.6	1.71	25.9	0.35	20.7	0.93
90	$C_7H_6^+$	2.14	3.01	1.38	0.12	1.11	2.24
84		0.04	0.04	0.04	0.13	0.05	0.04
83		...	0.01	...	1.63	...	...
82		0.01	0.03	...	0.29	0.01	0.04
81		0.05	0.12	0.01	0.50	0.01	0.18
80		0.14	0.66	0.14	1.09	0.18	2.57
79	$C_6H_7^+$	0.63	0.68	1.67	0.50	2.54	0.54
78		0.85	2.57	0.47	0.37	0.69	2.12
77	$C_6H_5^+$	3.37	0.96	1.78	0.13	2.66	0.73
70		0.01	0.01	...	0.12	0.01	...
69		0.01	0.01	0.01	2.30	0.01	...
68		0.03	0.05	0.01	6.60	0.01	0.02
67		0.08	0.68	0.03	3.93	0.03	0.49
66		1.04	9.52	0.68	1.69	0.67	8.70
65	$C_5H_5^+$	13.7	5.18	11.8	2.08	11.8	4.08
64		1.63	2.61	1.34	1.73	1.09	2.18
63		4.22	2.70	4.23	0.73	4.14	2.75
30	NO^+	2.53	2.60	2.52	2.71	3.05	3.05

		Metastable Peaks					
		ortho		*meta*		*para*	
Apparent mass	Transition	Unlabeled	α-d[b]	Unlabeled	2,4,5,6-d_4[c]	Unlabeled	α-d[b]
106.9	$(137^+) \rightarrow (121^+) + 16$	...	...	0.01	...	...	...
106.1	$(138^+) \rightarrow (121^+) + 17$	...	0.07	...	...	...	...
105.1	$(137^+) \rightarrow (120^+) + 17$	0.08	...	...	...	...	...
87.3	$(141^+) \rightarrow (111^+) + 30$	...	...	...	0.02	...	...
83.6	$(137^+) \rightarrow (107^+) + 30$	...	...	0.01	...	...	...
77.1	$(83^+) \rightarrow (80^+) + 3$	...	...	...	0.01	...	...
76.1	$(80^+) \rightarrow (78^+) + 2$	...	0.03	...	...	...	0.04
75.1	$(79^+) \rightarrow (77^+) + 2$	0.03	...	0.02	...	0.05	...
71.4	$(121^+) \rightarrow (93^+) + 28$	...	0.02	...	...	...	...
70.5	$(120^+) \rightarrow (92^+) + 28$	0.02	...	...	...	...	...
60.4	$(137^+) \rightarrow (91^+) + 46$	...	...	0.01	...	...	...
50.1	$(95^+) \rightarrow (69^+) + 26$	...	...	...	0.01	...	...
48.7	$(95^+) \rightarrow (68^+) + 27$	...	...	...	0.03	...	...
47.4	$(92^+) \rightarrow (66^+) + 26$	...	0.04	...	...	...	0.04
47.3	$(95^+) \rightarrow (67^+) + 28$	...	...	...	0.2	...	...
46.4	$(91^+) \rightarrow (65^+) + 26$	0.05	...	0.06	...	0.06	...
45.9	$(92^+) \rightarrow (65^+) + 27$	0.02	...	...	...	...	...

[a] Formulas are shown opposite masses of the appropriate unlabeled ions only. [b] Corrected for isotopic impurity. [c] Uncorrected for isotopic impurities: 4.4%–d_3, 0.1% –d_2, and 0.3% unlabeled.

Chart I. Decomposition Schemes for Isomeric Nitrotoluenes

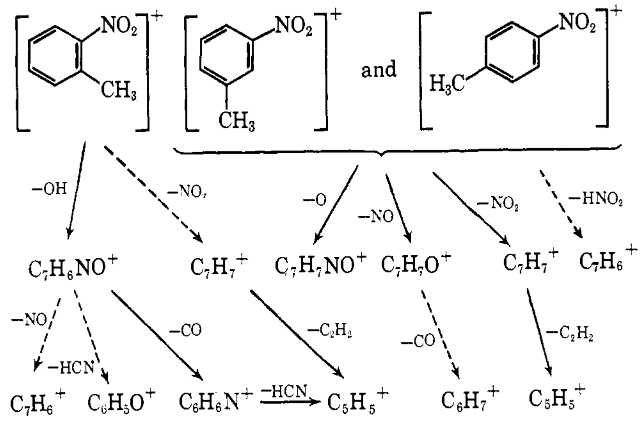


Table III. Partial Spectra of Nitrobiphenyls

Mass	Ion	Relative intensity ortho	meta	para
199	$C_{12}H_9NO_2^+$	2.23	18.8	16.2
184		0.05	0.04	0.07
183	$C_{12}H_9NO^+$	0.59	0.29	0.30
182	$C_{12}H_8NO^+$	3.47	0.01	0.06
171	$C_{11}H_9NO^+$	4.84	0.01	0.11
170		1.58	0.06	0.72
169	$C_{12}H_9O^+$	1.11	0.30	5.13
155		0.37	0.11	0.13
154	$C_{11}H_8N^+$	2.18	1.74	1.37
153	$C_{12}H_9^+$	1.99	13.9	6.78
152	$C_{12}H_8^+$	9.27	16.7	15.0
143	$C_{10}H_9N^+$	3.74	0.03	0.09
142		1.69	0.28	0.60
141	$C_{11}H_9^+$	2.19	2.08	4.68
30	NO^+	1.45	1.96	2.64

Metastable Peaks: Apparent mass	Transition	ortho	meta	para
166.5	$(199^+) \to (182^+) + 17$	0.05	...	...
151.0	$(153^+) \to (152^+) + 1$	0.11	0.65	0.44
146.9	$(199^+) \to (171^+) + 28$	0.02	...	...
143.5	$(199^+) \to (169^+) + 30$	...	0.01	0.04
119.6	$(171^+) \to (143^+) + 28$	0.03	...	...
117.6	$(199^+) \to (153^+) + 46$ $(169^+) \to (141^+) + 28$	0.03	0.05	0.03

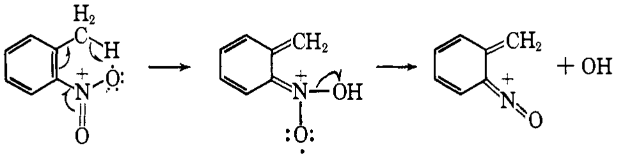
Table IV. Partial Spectrum of 4,5-Dimethoxy-2-nitrophenol

Mass	Ion	Probable origin	Rel intensity
199	$C_8H_9NO_5^+$	Parent ion	14.5
184	$C_7H_6NO_5^+$	199^+-CH_3	6.40
183			0.43
182	$C_8H_8NO_4^+$	199^+-OH	0.39
171	$C_7H_9NO_4^+$	199^+-CO	0.01
170			0.08
169	$C_7H_7NO_4^+$ $C_8H_9O_4^+$	199^+-CH_2O 199^+-NO	0.85
156	$C_6H_6NO_4^+$	184^+-CO	0.19
155	$C_7H_7O_4^+$	182^+-HCN	0.04
154	$C_7H_8NO_3^+$	182^+-CO	0.19
153	$C_8H_9O_3^+$	199^+-NO_2	0.68
152			
141	$C_6H_7NO_3^+$ $C_7H_9O_3^+$	169^+-CO	1.34 0.30
126	$C_5H_4NO_3^+$ $C_6H_6O_3^+$	141^+-CH_3	0.77
125	$C_7H_9O_2^+$	153^+-CO	1.90
30	NO^+		2.58

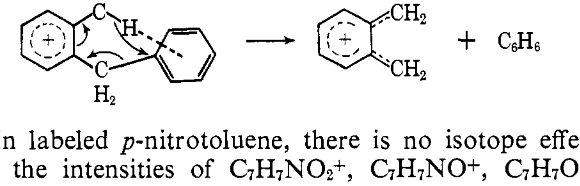
Metastable Peaks: Apparent mass	Transition	Rel intensity
170.1	$(199^+) \to (184^+) + 15$	0.06
117.6	$(199^+) \to (153^+) + 46$ $(169^+) \to (141^+) + 28$	0.06
112.6	$(141^+) \to (126^+) + 15$	0.01
102.1	$(153^+) \to (125^+) + 28$	0.01

and this inference is confirmed by the spectrum of the *α-d* species. In contrast to the analogous data in the spectrum of *o*-methyl-*d*-diphenylmethane,[20] the present spectrum shows pronounced isotope effects. A deuterium atom in the methyl group apparently opposes primary loss of OH to form $C_7H_6NO^+$ and also stabilizes this ion, once formed, against further decomposition to $C_6H_5O^+$ and $C_6H_6N^+$. The first effect can account for the enhanced intensity of the parent ion; the second, for the reduced intensity ratio of $C_6H_5DN^+:C_7H_5DNO^+$ (mass 93:mass 121), as compared with that of the corresponding ions in the spectrum of the unlabeled compound; the two effects together, for the essentially unchanged intensity of $C_7H_6NO^+$ (including the labeled ion). Label retention in $C_7H_6NO^+$ is 81%, substantially higher than the 67% that would be expected on a purely random statistical basis. Thus, the observed yield of this ion also reflects the counterbalancing effects of an increase in strength of the C–D bond and weakening of the methyl C–H bonds as compared with the corresponding bonds in the unlabeled molecule.[28]

The occurrence of an easily detectable isotope effect on primary loss of OH from *o*-nitrotoluene-*α-d* implies that the reaction mechanism differs from the formally similar loss of C_6H_6 from *o*-methyl-*d*-diphenylmethane.[20] The stretching, or perhaps breaking, of the C–H bond is apparently far more advanced in the transition state for the former than for the latter reaction. The nitrotoluene reaction may well occur *via* a discrete intermediate.



In contrast, the *o*-methyldiphenylmethane reaction is perhaps best represented in terms of (a) formation of a loose *π*- or *σ*-type hydrogen bond; (b) rupture of the C–C bond as the rate-determining step; and (c) fast transfer of the hydrogen atom as the transition state collapses to products.



In labeled *p*-nitrotoluene, there is no isotope effect on the intensities of $C_7H_7NO_2^+$, $C_7H_7NO^+$, $C_7H_7O^+$, $C_7H_7^+$, $C_6H_7^+$, and probably $C_5H_5^+$. The yield of labeled $C_5H_5^+$ agrees closely with that expected if the ion is assumed to arise solely by loss of C_2H_2 from $C_7H_7^+$,

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[28] D. P. Stevenson and C. D. Wagner, *J. Chem. Phys.*, **19**, 11 (1951); D. P. Stevenson, *ibid.*, **19**, 17 (1951).

and if H and D atoms in labeled $C_7H_7^+$ are equivalent.[22] The absence of isotope effects is consistent with the postulated decomposition reactions, none of which requires cleavage of a methyl C–H bond, except for the presumed ring-expansion step in which $C_7H_7^+$ attains the symmetrical tropylium configuration. In the *meta* isomer, also, spectral intensities of the labeled species parallel closely those of the unlabeled species, with no suggestion of isotope effects.

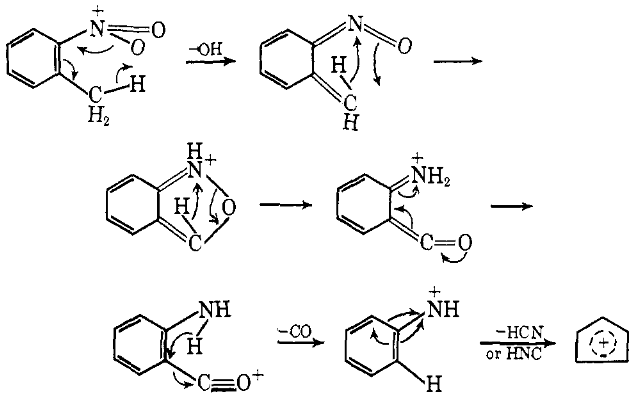
A. Voltage-Dependence Measurements. In the mass 120 region of the spectrum of *o*-nitrotoluene at 7.0 to 8.0 ionizing volts (uncorrected), the ion yield, beyond a trace of $C_7H_7NO^+$, consists of about 5% $C_7H_5NO^+$ and 95% $C_7H_6NO^+$. Label retention in $C_7H_6NO^+$ in the spectrum of the labeled species is ~88%, *vs.* 81% at 70 v. This voltage dependence suggests a situation similar to that in the loss of hydrogen atom from the toluene ion. That reaction occurs from two discrete states of the $C_7H_8^+$ ion, which are characterized by different appearance potentials, different half-lives, and—when deuterated species are used—different isotope effects.[29]

The high label retention in $C_7H_6NO^+$ may be due in some small measure to participation of ring hydrogen in the process by which OH is lost. Ion intensity corresponding to loss of OH—although, admittedly, this ion may arise by successive loss of O and H—in the spectra of the *meta* and *para* isomers is extremely low. But, as nearly as can be judged from the spectrum of *m*-nitrotoluene-2,4,5,6-d_4, the four ring deuterium atoms and the three methyl protiums contribute statistically to this process. Although the mechanism is not clear, such a process may also contribute in the *ortho* isomer.

In the mass 91 to 93 region at 7.0 to 8.0 ionizing volts (uncorrected), the ion yield consists of about 8% $C_6H_6N^+$ and 92% $C_6H_5O^+$, the products of respective loss of CO and HCN from $C_7H_6NO^+$. Label retention in $C_6H_5O^+$ in the spectrum of the labeled species is ~33%, *vs.* 50% at 70 v. Clearly, the hydrogen atom lost as HCN comes chiefly, if not solely, from the methyl group. Retention in this ion near the appearance potential is surprisingly low, as though the overall reaction sequence by which it arises were free of isotope effects. Apparently, secondary loss of HCN (including DCN in the labeled species) is more likely to occur in a $C_7H_6NO^+$ ion free of deuterium than in a labeled one.

In measurements on the labeled species, $C_5H_5^+$ suffers interference from $C_5H_4^+$ and $C_5H_6^+$. However, taking these into account, we estimate that ~50% of the $C_5H_5^+$ ions retain the label over the range of 10.6 to 12.2 ionizing volts (uncorrected) *vs.* ~65% at 70 v. The $C_5H_5^+$ yield contains contributions from two reaction paths: (1) sequential loss of OH, CO, and HCN; (2) sequential loss of NO_2 and C_2H_2. Reducing the ionizing voltage evidently favors path 1 at the expense of 2, as would be expected on thermochemical grounds if the $C_5H_5^+$ ions arising by the two paths have the same structure. Hydrogen loss in the second step of 2 presumably occurs randomly from all positions.[22] In 1, the hydrogen atom lost in the first step certainly comes from the methyl group; and apparently that lost in the third step also comes from this position, preferentially if not exclusively. After loss of OH, one or both of the remaining methyl hydrogens must migrate to the nitrogen atom. Perhaps a rough analogy is justified with loss of HCN from aniline under electron impact, in which at least 68% of the H atoms lost originate in the amino group.[30a]

The sequential loss of OH, CO, and HCN can thus be pictured as



This scheme is consistent with both the present deuterium-labeling evidence and the finding from ^{13}C-labeling[12] that the carbon atom lost as CO is the methyl carbon. The hydrogen and oxygen migrations shown—effectively an intramolecular oxidation–reduction—resemble postulated reactions of N,N-diarylacetamides under electron impact;[30b] the photochemical rearrangements of nitrones to amides[15] and of *o*-nitrobenzyl alcohol and *o*-nitrobenzaldehyde to *o*-nitrosobenzaldehyde and *o*-nitrosobenzoic acid, respectively;[14] and thermal rearrangements of *o*-nitrotoluene, *o*-nitrobenzyl alcohol, and *o*-nitrophenylmethanethiol to anthranilic acid, *o*-aminobenzaldehyde, and thioanthranil, respectively.[14] The present deuterium-labeling data parallel closely, in a different context, the recently reported photochemical hydrogen abstraction by the nitro group in *o*-nitrotoluene.[31]

B. Nitro–Nitrite Isomerization and Subsequent Loss of CO. Isomerization of the nitroarene parent ion to the aryl nitrite configuration, required by the observed primary loss of NO, parallels the isomerization of sulfone parent ions in the mass spectrometer to sulfinate esters[19,32] and that of phenyldixylylphosphine oxide—presumably other phosphine oxides behave similarly—to phenylxylylxylyloxyphosphine.[33] Similar isomerizations apparently occur in the photochemical formation of 10,10′-dianthronyl from 9-nitroanthracene,[34] 1-phenyl-1-oximinopropan-2-one from β-methyl-β-nitrostyrene,[35] and 3-oximinocholest-4-en-6-one from 6-nitrocholesta-3,5-diene;[35] and in the thermal conversion of tetraalkyl hypophosphates to esters of phosphorous–phosphoric anhydrides[36] and of N-nitrosoacetanilides to

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(29) A. G. Harrison, T. W. Shannon, and F. Meyer, *Advan. Mass Spectr.*, 3, 377 (1966).

(30) (a) P. N. Rylander, S. Meyerson, E. L. Eliel, and J. C. McCollum, *J. Am. Chem. Soc.*, **85**, 2723 (1963); (b) P. Funke, K. G. Das, and A. K. Bose, *ibid.*, **86**, 2627 (1964).

(31) H. Morrison and B. H. Migdalof, *J. Org. Chem.*, 30, 3996 (1965).

(32) S. Meyerson and J. D. McCollum, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1959, Abstracts, p 29S.

(33) S. Meyerson, unpublished results.

(34) R. D. Campbell and R. F. Ofstead, private communication.

(35) O. L. Chapman, P. G. Cleveland, and E. D. Hoganson, *Chem. Commun.*, 101 (1966). These authors have called attention to possible implications of mass spectra of nitroarenes for mechanisms of photochemical reactions.

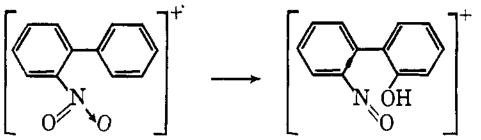
(36) J. Michalski, W. Stec, and A. Zwierzak, *Chem. Ind.* (London), 347 (1965).

diazonium acetates.[37] The photochemical isomerization of nitromethane to methyl nitrite has been suggested,[38] although later work led to the proposal that methyl nitrite arises not in an intramolecular rearrangement but by recombination of CH_3 and NO_2 radicals formed in the primary photolytic process.[39–41]

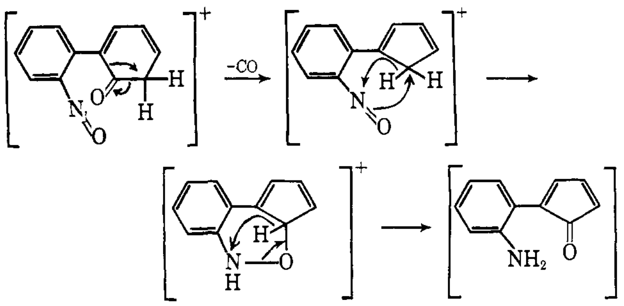
The ions occurring at mass 79 in the spectra of the three unlabeled nitrotoluenes are displaced quantitatively in those of the labeled species. Thus, none of the original deuterium atoms and, almost certainly, no hydrogen is lost in forming these ions. The labeling data thereby independently confirm the over-all reaction—loss of NO and CO—reported by Beynon and co-workers[10] on the basis of metastable peaks and high-resolution mass measurements. Loss of CO is a known, apparently characteristic reaction of aryloxy ions. It has been reported to occur following primary loss of CH_3 from a variety of methoxyarenes[19,42–47] and loss of arylsulfoxy radicals from arenesulfinate ions derived from diaryl sulfones.[19]

Nitrobiphenyls and Dimethoxy-2-nitrophenol. Steric and Mesomeric Effects. The nitrobiphenyl and dimethoxy-2-nitrophenol spectra show a number of noteworthy features that can be rationalized in terms of steric and mesomeric effects.

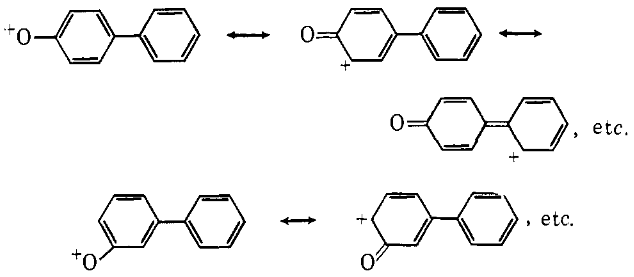
Intensity at the parent mass less 17 units—due to loss of OH—is substantial in the spectrum of *o*-nitrobiphenyl, even though not as prominent as in that of *o*-nitrotoluene. Evidently, a sterically accessible ring hydrogen atom can participate in this reaction despite being more tightly bound than a benzylic hydrogen. The comparatively low intensity of the product ion from this reaction may be due in part to competition from another reaction path unique to the *ortho* isomer among the nitrobiphenyls and not observed in *o*-nitrotoluene—sequential loss of two molecules of CO. The primary decomposition step in this path suggests isomerization of the parent ion to 2-(2′-nitrosophenyl)-phenol.



The nitrosophenylphenol structure, like phenol itself,[4] would be expected to lose CO *via* a cyclohexadienone intermediate. This decomposition step is evidently accompanied by the making of a new C–O bond, as in nitrotoluene laying the groundwork for subsequent loss of a second molecule of CO. Primary loss of CO from *o*-nitrobiphenyl resembles closely the recently reported[12b] loss of CO from 1-nitronaphthalene, which involves migration of an oxygen atom to C-8. Subsequent loss of a second molecule of CO is observed there also, although less prominently than in the biphenyl.



Intensity at the parent mass less 30—due to loss of NO—is far higher in the spectrum of *p*-nitrobiphenyl than in that of the *meta* isomer. This pattern resembles that of the corresponding nitrophenols and, to a lesser extent, the nitroanilines rather than the nitrotoluenes. The explanation most likely lies in the greater resonance stabilization available to the phenylphenoxy ion derived from the *para* isomer, by virtue of interaction with the second phenyl ring, than to that derived from the *meta* isomer.



Similarly enhanced resonance stabilization in the *p*-amino- and *p*-hydroxyphenoxy ions is presumably largely responsible for differences between the spectra of the *meta* and *para* isomers of nitroaniline and nitrophenol.

The intense peaks at mass 152 in the spectra of all three nitrobiphenyls correspond to $C_{12}H_8^+$, which is shown by metastable peaks to arise by successive loss of NO_2 and H. Most likely, this is a biphenylene ion, formed directly in breakdown of the *ortho* isomer and perhaps *via* a phenylbenzyne intermediate in that of the *meta* and *para* isomers. Phenylbenzyne ions almost certainly do not have localized double and triple bonds; thus the three isomers form biphenylene with about equal ease.

In the spectrum of 4,5-dimethoxy-2-nitrophenol, the features characteristic of nitroarenes, and particularly of *ortho*-substituted nitroarenes, do not stand out prominently, but are obscured by products of reactions involving the other substituents. The most abundant fragment ion arises by loss of CH_3, suggesting that a methoxy group is the preferred center of reactivity and presumably of charge localization in the parent ion. Preferred charge localization in the methoxy group has been proposed[22] to account for survival of the aromatic skeletal structure in the *m*- and *p*-$CH_3OC_6H_4CH_2^+$ ions derived from the corresponding methoxybenzyl halides,

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(37) D. F. DeTar, *J. Am. Chem. Soc.*, **73**, 1446 (1951); R. Huisgen and L. Krause, *Ann.*, **574**, 157, 171 (1951).

(38) H. W. Brown and G. C. Pimentel, *J. Chem. Phys.*, **29**, 883 (1958).

(39) G. C. Pimentel and G. Rollefson in "Formation and Trapping of Free Radicals," A. M. Bass and H. P. Broida, Ed., Academic Press Inc., New York, N. Y., 1960, Chapter 4.

(40) R. E. Rebbert and N. Slagg, *Bull. Soc. Chim. Belges*, **71**, 709 (1962).

(41) B. H. J. Bielski and R. B. Timmons, *J. Phys. Chem.*, **68**, 347 (1964).

(42) G. Spiteller and M. Spiteller-Friedmann, *Monatsh.*, **93**, 1395 (1962).

(43) C. S. Barnes and J. L. Occolowitz, *Australian J. Chem.*, **16**, 219 (1963).

(44) Z. Pelah, J. M. Wilson, M. Ohashi, H. Budzikiewicz, and C. Djerassi, *Tetrahedron*, **19**, 2233 (1963).

(45) Reference 7, p 140.

(46) G. R. Waller, R. Ryhage, and S. Meyerson, *Anal. Biochem.*, in press.

(47) D. M. Clugston and D. B. MacLean, *Can. J. Chem.*, **44**, 781 (1966).

in contrast to ring expansion in the hydroxy, methyl, and fluoro analogs to form substituted tropylium ions.[48] Similarly, the apparently greater ability of the methoxyl than of the hydroxyl group to stabilize the charge is reflected in a pronounced shift of charge retention between complementary products upon replacing the hydroxyl group on C-3 of 4,6-dideoxy-D-xylohexose dithioacetal with methoxyl;[49] and the intensities of the substituted benzoylium ions in the spectra of neopentyl *p*-methoxy- and *p*-nitrobenzoates are, respectively, increased and decreased relative to the unsubstituted ester, in accord with the charge-stabilizing and -destabilizing effects of the substituents.[50]

Consideration of the spectra of the isomeric nitrobiphenyls and the dimethoxynitrophenol emphasizes the importance of charge distribution and stabilization in directing the decomposition reactions of ionized molecules. Functional groups that serve as preferred sites for charge localization or that interact with other parts of the molecule to alter its ability to accommodate the charge can thus exert profound effects on mass spectra. In favorable cases, correlation of selected spectral features with Hammett or related substituent constants has been good enough to serve as a basis for quantitative prediction.[11,23] In view of the large number of competing and consecutive reactions contributing to the mass spectra of nitroarenes, the attainment of correlations adequate for such prediction seems unlikely. Nonetheless, these concepts can be highly useful in rationalizing differences among the spectra of isomers, and conversely, one would hope, in assigning probable isomeric structures when sufficient spectral data are available.[51]

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[48] J. M. S. Tait, T. W. Shannon, and A. G. Harrison, *J. Am. Chem. Soc.*, **84**, 4 (1962).

[49] D. C. DeJongh and S. Hanessian, *ibid.*, **88**, 3114 (1966).

[50] W. H. McFadden, K. L. Stevens, S. Meyerson, G. J. Karabatsos, and C. E. Orzech, *J. Phys. Chem.*, **69**, 1742 (1965).

[51] Note Added in Proof. Two additional relevant papers have appeared very recently: J. Harley-Mason, T. P. Toube, and D. H. Williams, *J. Chem. Soc.*, B396 (1966); T. H. Kinstle, J. R. Althaus, and J. Stam, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstracts, p S-141. As reported in the latter paper, the mass spectra of β-nitrostyrenes show primary loss of OH and of CO, in close analogy to *o*-nitrobiphenyl.

Studies in Mass Spectrometry. XIX.[1] Evidence for the Occurrence of Aromatic Substitution Reactions upon Electron Impact

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Received June 20, 1966

Abstract: The mass spectra of a number of compounds of the general formula $C_6H_5CH{=}CHCOR$ contain intense M − 1 peaks, which largely arise through the loss of a hydrogen atom from the aromatic ring. Selective deuteration experiments suggest that the phenyl hydrogens become equivalent in the molecular ion. The M − 1 species is probably formed *via* an intramolecular aromatic substitution reaction which can occur in the molecular ion and results in the formation of a relatively stable benzopyrylium cation.

In investigations of the behavior of β-keto esters,[2] β-diketones,[3] and enamines[4] upon electron impact we have uncovered reactions which are believed to correspond to intramolecular substitution reactions occurring in the mass spectrometer. Thus, ethyl 3-(2′,4′,6′-d_3-phenylamino)but-2-enoate (I) was shown to eliminate C_2H_5DO and C_2H_6O from its molecular ion in the ratio 85:15, and the loss of a deuterium atom from the aromatic ring was rationalized in terms of an intramolecular acylation of the aromatic ring by the acylium ion a to give the stabilized quinolinium ion b *via* loss of a deuterium atom.[4] Similarly, the successive losses of C_2H_5O, H, and C_2H_6O (as established by appropriate metastable peaks) from diethyl benzoylmalonate (II) demanded the elimination of an aromatic hydrogen atom to form the final ion, which was formulated as e.[2] Once more, it seemed reasonable that the driving force for the elimination of an aromatic hydrogen might be the intramolecular "Friedel–Crafts acylation" of the aromatic ring in the acylium ion c; ethanol could then be eliminated from d to furnish e.

The second type of aromatic substitution reaction which we have suggested may occur upon electron impact involves the formation of a completely aromatic benzopyrylium ion.[3] Thus, dibenzoylmethane (III) exhibits a pronounced M − H ion in its spectrum, which still corresponds to the loss of a hydrogen atom from the molecular ion in the spectrum of the d_2 derivative IV. It was concluded that the driving force for the loss of the aromatic hydrogen atom, which is of necessity eliminated in the formation of the M − 1 species, lay in the formation of the oxonium ion f[3] from a molecular ion IIIa of III.

Reactions which bear some analogy to our sugges-

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[1] Part XVIII: J. T. B. Marshall and D. H. Williams, *Tetrahedron*, in press.

[2] J. H. Bowie, D. H. Williams, S.-O. Lawesson, and G. Schroll, *J. Am. Chem. Soc.*, **87**, 5742 (1965).

[3] J. H. Bowie, D. H. Williams, S.-O. Lawesson, and G. Schroll, *J. Org. Chem.*, **31**, 1384 (1966).

[4] H. J. Jakobsen, S.-O. Lawesson, J. T. B. Marshall, G. Schroll, and D. H. Williams, *J. Chem. Soc.*, in press.