Mass Spectral and Thermal Reactions of Dinitrobenzenes

ELLIS K. FIELDS* AND SEYMOUR MEYERSON

Amoco Chemicals Corporation, Naperville, Illinois 60540, and Standard Oil Company, Naperville, Illinois 60540

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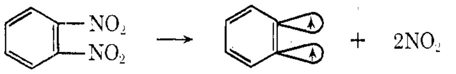
Thermal reactions of dinitrobenzenes can be explained in terms of initial decomposition to NO_2 and nitrophenyl radicals, paralleling primary loss of NO_2 in the mass spectrum. To some extent the nitrophenyl radicals in turn lose NO_2 and give products formally derived from phenylene diradicals. *o*-Dinitrobenzene gives naphthalene derivatives with benzene-d_6 and hexafluorobenzene, suggesting some concerted loss of NO_2 groups to yield benzyne. Formation of benzofurazan both in the mass spectrum and among thermal reaction products of *o*-dinitrobenzene points to interaction between the nitro groups in this isomer.

Nitrobenzene at 600° decomposes to phenyl radical and NO_2.[1] Similar fragmentation of dinitrobenzenes

$$C_6H_5NO_2 \longrightarrow C_6H_5\cdot + NO_2\cdot$$

should give products formally derived from phenylene diradicals. In particular, concerted decomposition of *o*-dinitrobenzene should yield benzyne, perhaps as a diradical, a species for which little evidence thus far has been found in either liquid or gas phase.



In view of the many known parallels between reactions induced by electron impact and thermally, and of the demonstrated usefulness of the former as a guide to the latter,[1] we initiated this work by measuring and studying the mass spectra of the three isomeric dinitrobenzenes. A mass spectrum of only one, the para isomer, has been reported,[2] and our spectrum of this isomer is in good qualitative agreement with the earlier one. Thermal reactions were run at 500–650° with benzene, benzene-d_6, and hexafluorobenzene. In addition, the products of reaction of *m*-dinitrobenzene with pyridine, thiophene, and three substituted benzenes at 550° were compared to find any significant variation.

Experimental Section

The reagents and standards for gas chromatography were purchased from Aldrich and purified, where necessary, by distillation, crystallization, and gas chromatography.

Mass spectra were measured on a modified Consolidated Model 21-103 instrument at 70 eV, with the sample-introduction system and ionization chamber both at 250°. Spectra were measured at the conventional 70 eV and at low voltage, 7.5 eV nominal, except that of the product mixture from reaction of *o*-dinitrobenzene and hexafluorobenzene, which was measured at 9.5 eV to increase sensitivity and thereby facilitate measurement of peak intensities for the large number of low-level components present. For the low-voltage measurements, the repellers were maintained at an average potential of 3 V, the exact values being selected to give maximum sensitivity. Relative intensities in the low-voltage spectra of product mixtures were taken as a first approximation to relative concentrations;[3] in the spectra of labeled materials, they were used for isotopic analysis. Directly coupled gas chromatography–mass spectrometry[4] was used as needed for qualitative identification of products, and gas chromatography, usually on a column of polyethylene glycol sebacate on Chromosorb W, for quantitative analysis.

In a typical experiment, a solution of 16.8 g (0.1 mol) of *m*-dinitrobenzene in 88.88 ml (1 mol) of benzene was pumped into a Vycor tube filled with Vycor chips under nitrogen flowing at 10 cc/min. The tube temperature was 550 ± 4°. Pumping rate was such as to give a contact time in the hot tube of 15 sec. Condensate from the tube was distilled to remove most of the benzene until the pot temperature was 120°; the residue, 25.4 g, was analyzed by gas chromatography with the results shown in Table I.

TABLE I

REACTIONS OF DINITROBENZENES WITH BENZENE[a]

Products	Wt %[b] Ortho, 12.5[c]	Meta, 25.4[c]	Para, 12.1[c]
Nitrobenzene	5.9	1.0	0.4
Phenol	3.1	8.3	14.5
Naphthalene	0.9	0.8	1.0
Biphenyl	46.0	60.4	67.2
Dibenzofuran	2.5	2.3	1.6
Dinitrobenzene	6.6	2.3	0.5
2-Nitrobiphenyl	21.5		
3-Nitrobiphenyl		1.3	
4-Nitrobiphenyl			1.7
2-Hydroxybiphenyl	2.7	0.1	
3-Hydroxybiphenyl		5.2	
4-Hydroxybiphenyl	0.7	0.5	3.2
o-Terphenyl	4.5	1.1	0.2
m-Terphenyl	1.2	10.3	1.0
p-Terphenyl	1.1	2.3	3.4
Unknowns	3.3	4.1	5.3

[a] Conditions: 0.1 mol of dinitrobenzene, 1 mol of benzene; 550°; contact time, 15 sec; N_2, 10 cc/min. [b] Determined by gas chromatygraphy. [c] Total weight of products, grams.

Results and Discussion

Mass Spectral Reactions.—Mass spectra of the dinitrobenzenes are listed in Table II; intensities are expressed in terms of per cent of total ion intensity at masses 26 to 170, inclusive. Partial decomposition schemes deduced from the spectra are shown in Schemes I and II. Wherever a metastable peak was found by us, or is reported elsewhere,[2] to support a postulated decomposition step, a solid arrow is used; otherwise the arrow is broken. The nominal mass and, in parentheses, intensity are shown below each ion formula.

The mass differences characterizing these spectra coincide generally with those found in the spectra of other nitroarenes;[2,5] similar processes are evidently involved. Also paralleling observations on other sets of nitroaromatic isomers are the close similarity of the spectra of *m*- and *p*-dinitrobenzenes and the pronounced differences between them and that of the ortho isomer.[2,5]

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[1] (a) E. K. Fields and S. Meyerson, *Accounts Chem. Res.*, **2**, 273 (1969); (b) *Intra-Sci. Chem. Rep.*, **3**, 219 (1969).

[2] J. H. Beynon, R. A. Saunders, and A. E. Williams, *Ind. Chim. Belge*, **29**, 311 (1964).

[3] E. K. Fields and S. Meyerson, *J. Org. Chem.*, **35**, 62 (1970).

[4] R. S. Gohlke, *Anal. Chem.*, **31**, 535 (1959); L. P. Lindeman and J. L. Annis, *ibid.*, **32**, 1742 (1960); J. T. Watson and K. Biemann, *ibid.*, **36**, 1135 (1964).

[5] S. Meyerson, I. Puskas, and E. K. Fields, *J. Amer. Chem. Soc.*, **88**, 4974 (1966).

TABLE II

MASS SPECTRA OF DINITROBENZENES[a]

M/z	Ortho	Meta	Para	Metastable transitions
26	0.64	0.43	0.55	
27	0.92	0.51	0.36	
28	0.95	0.80	0.95	
29	0.22	0.21	0.24	
30	26.7	17.2	21.3	
31	0.12	0.09	0.11	
32	0.06	0.04	0.04	
32.9 (m[b])	0.01	0.02	0.01	$76^+ \rightarrow 50^+ + 26$
36	0.11		0.12	
37	1.41	1.19	1.29	
37.5 (d[c])	0.01	0.01	0.01	
38	2.83	1.92	2.06	
38.5 (d)	0.01	0.01		
39	5.16	1.48	1.11	
40	0.53	0.16	0.13	
41	0.09	0.04	0.04	
42	0.11	0.03	0.04	
43	0.05	0.03	0.03	
43.5 (d)	0.01	0.01	0.01	
44	0.32	0.16	0.34	
44.5 (m)	0.003	0.01	0.01	$92^+ \rightarrow 64^+ + 28$
45	0.10	0.08	0.06	
46	0.95	0.75	0.68	
48	0.05	0.05	0.05	
49	0.52	0.49	0.48	
50	10.0	11.4	11.3	
51	3.31	1.59	1.33	
52	1.85	0.60	0.51	
53	2.16	0.30	0.61	
54	0.16	0.16	0.22	
55	0.05	0.19	0.03	
56		0.03		
60	0.07	0.07	0.09	
61	0.39	0.47	0.56	
62	0.71	0.70	0.96	
62.0 (m)	0.09	0.03	0.04	$64^+ \rightarrow 63^+ + 1$
63	6.94	2.65	2.72	
64	6.37	3.00	3.18	
65	0.48	0.30	0.29	
66	0.34	0.15	0.11	
67	0.18	0.05	0.04	
68	0.24	0.03	0.07	
69	0.03			
69.4 (m)		0.01	0.01	$122^+ \rightarrow 92^+ + 30$
72	0.03	0.03	0.04	
73	0.39	0.54	0.61	
74	2.50	3.50	3.88	
75	2.03	10.8	11.73	
76	3.84	11.2	9.18	
77	0.88	0.96	0.80	
78	1.03	0.16	0.07	
79	0.13	0.12	0.05	
80	1.11	0.07	0.06	
81	0.07			
82			0.07	
86	0.03	0.03	0.03	
87	0.05	0.07	0.08	
88	0.06	0.05	0.08	
89	0.02	0.02	0.04	
90	0.54	0.08	0.07	
91	0.12	0.16	0.11	
92	1.66	5.82	3.64	
93	0.19	0.45	0.29	
94	0.72	0.04	0.03	
95	0.07			
96			0.02	
103	0.03			
104	0.14	0.02	0.03	
105	0.03	0.03	0.06	
106		0.08	0.18	
107		0.13	0.03	
108	0.03	0.04	0.09	
120	0.50	0.02		
121	0.05	0.04	0.03	
122	0.41	4.76	4.12	
123	0.03	0.34	0.29	
124		0.03	0.03	
136	0.10			
137	0.03			
138	0.07	0.21	0.11	
139		0.02		
150		0.02	0.02	
152	0.24	0.63	0.57	
153	0.02	0.04	0.04	
168	6.98	11.0	10.3	
169	0.52	0.82	0.77	
170	0.07	0.12	0.11	

[a] Not corrected for naturally occurring heavy isotopes. [b] m denotes a metastable peak. [c] d denotes a peak attributed to a doubly charged ion.

Parent-peak intensity is markedly lower in the spectrum of the ortho isomer than of the others and, together with other differences distributed through the spectra, would seem to reflect the lower thermochemical stability of the ortho isomer.[6] Ions of lower mass in mass spectra are, in general, more likely than heavier ones to arise *via* multistep decomposition processes. Thus, the average masses of all ions in the spectra of related compounds can furnish a crude measure of the relative extents of decomposition. The values derived from the spectra in Table II follow: ortho, 60.5; meta, 75.1; and para, 71.5. Differences in thermochemical stability are evidenced by the heats of combustion[7]—ortho, −703.2; meta, −694.7; para, −692.0 kcal/mol—and by relative decomposition rates as neat liquids at 300°[8]—ortho, 6.8; meta, 1.0; para, 0.38%/hr.

More specifically, several of the strongest peaks in the spectra of the meta and para isomers—at masses 122, 92, 76, and 75—are far less intense in that of the ortho isomer. The differences seem compatible with only two possible explanations. The reaction paths involving the ions of these masses may play a less dominant role in the decomposition of the ortho isomer because of competition with alternative paths, or these ions when formed from the ortho isomer may contain more excess energy, which leads to more extensive decomposition in subsequent reaction steps. That the first of these alternatives is at least a factor is implied by a series of small peaks at masses 136, 120, and 104, corresponding to the loss of two, three, and four oxygen atoms from the molecular ion of the ortho isomer alone. The relative contributions of molecular and atomic

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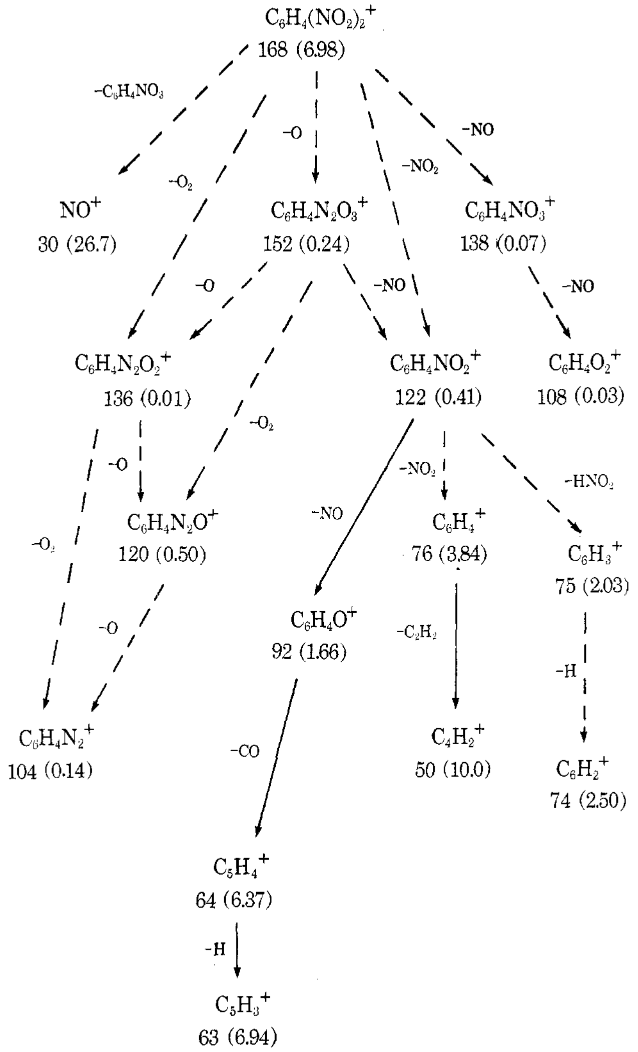
[6] For parallel effects in the mass spectra of stereoisomers, see S. Meyerson and A. W. Weitkamp, *Org. Mass Spectrom.*, **1**, 659 (1968); **2**, 603 (1969).

[7] M. S. Kharasch, *J. Res. Nat. Bur. Stand.*, **2**, 359 (1929).

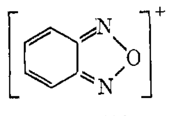
[8] J. C. Hoffsommer, private communication.

SCHEME I

PARTIAL DECOMPOSITION SCHEME FOR *o*-DINITROBENZENE UNDER ELECTRON IMPACT



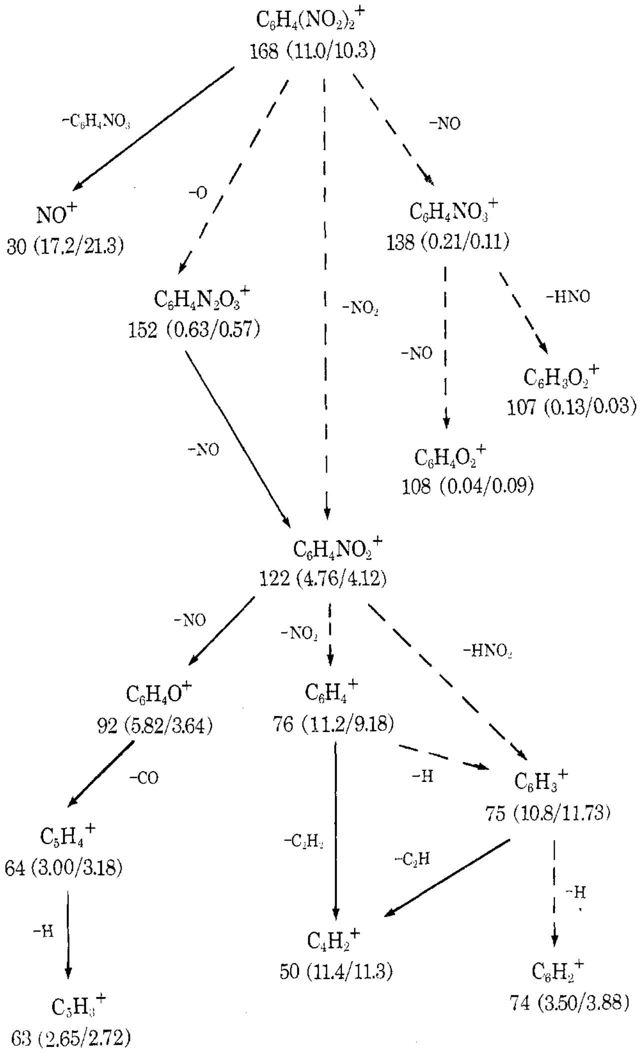
oxygen losses in the formation of these ions are not clear, but interactions of some sort between the neighboring substituents are evidently involved. The products may be stabilized by ring formation, as, for example, for the species of mass 120. Substituted benzofurazans have been isolated in low yields from thermal reactions of polynitro aromatic compounds.[8–10] Similarly, ions of masses 136 and 120 in the mass spectrum of *o*-nitrophenyl azide have been pictured with the structure of benzofuroxan and benzofurazan, respectively, also paralleling the known thermolysis of *o*-nitrophenyl azide to benzofuroxan.[11]



mass 120

SCHEME II

PARTIAL DECOMPOSITION SCHEME FOR *m*- AND *p*-DINITROBENZENES UNDER ELECTRON IMPACT (META/PARA)



Thermal Reactions.—The reaction products of the three dinitrobenzenes with benzene at 550° are shown in Table I. To clarify the origins of these products, we treated the dinitrobenzenes with benzene-d_6; to answer some pertinent questions, we used different temperatures for the various isomers. *m*-Dinitrobenzene was allowed to react at 500° to minimize thermal scrambling of protium and deuterium; the isotopic compositions of original and recovered benzenes are identical, showing there was no detectable exchange. A higher temperature seemed desirable for the ortho isomer. A larger amount of the nitrobiphenyl from *o*-dinitrobenzene survived at 550° than from the other two isomers. To induce a possible concerted loss of both nitro groups—or at least in quick enough succession to avoid interruption of the sequence by arylation—we ran its reaction with benzene-d_6 at 650°. For comparison, *p*-dinitrobenzene was treated with benzene-d_6 under the same conditions as the ortho isomer.

The reactions in Scheme III, with *m*-dinitrobenzene as model, can account for the products listed in Tables I and III. The reaction steps postulated here all have known close analogs in the pyrolysis of nitrobenzene.[1b] The symbol Ph is used to denote a benzene ring or

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(9) J. C. Hoffsommer, "Thermal Stability of Polynitropolyphenyl Compounds at Elevated Temperatures," Report NOLTR 67-118, U. S. Naval Ordnance Laboratory, Silver Spring, Md., July 28, 1967.

(10) J. C. Hoffsommer, "Thermal Stability of Polynitroaromatic Amines," Report NOLTR 65-227, U. S. Naval Ordnance Laboratory, Silver Spring, Md., Feb. 16, 1966.

(11) R. A. Abramovitch, E. P. Kyba, and E. F. V. Scriven, *J. Org. Chem.*, **36**, 3796 (1971).

TABLE III

REACTIONS OF DINITROBENZENES WITH BENZENE-d_6[a]

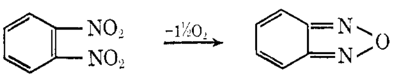
Product	No. of D atoms	Isotopic distribution, %[b] Ortho, 650°	Meta, 500°	Para, 650°	Summed relative intensity[c] Ortho, 650°	Meta, 500°	Para, 650°
Benzene	0	1.0		10.3			
	1	0.4					
	2	0.4					
	3	0.2					
	4	1.0					
	5	8.6	3.6	8.1			
	6	88.4	96.4	81.6	47.0	20.3	4.4
Phenol	0	25	43	11			
	1	16	29				
	2	28	28	14			
	3	19		22			
	4	12		36			
	5			17	3.2	0.8	1.8
Nitrobenzene	0		14				
	1		72				
	2		14			2.1	
Naphthalene	4	25					
	5	25					
	6	12					
	7	13					
	8	25	100	100	1.6	0.4	0.5
Biphenyl	0		1.8				
	1						
	2						
	3						
	4						
	5	1.9		0.3			
	6	8.8	0.9	1.8			
	7	5.1	4.5	2.7			
	8	3.2	1.8	3.8			
	9	12.3	0.8	4.2			
	10	68.7	90.2	87.2	37.4	41.0	76.9
Dinitrobenzene	0		100			1.5	
Hydroxybiphenyl[d]	2		6				
	3		10	9			
	4		10	24			
	5	50	21	47			
	6	50	53	20	0.4	3.5	1.4
Nitrobiphenyl	4		2				
	5		85				
	6		13			17.7	
Terphenyl	9			2			
	10	22	48	10			
	11	15	24	14			
	12	15	4	16			
	13	13		18			
	14	35	24	40	4.6	4.6	12.6

[a] Conditions: 0.01 mol of dinitrobenzene, 0.1 mol of benzene-d_6; isotopic composition of benzene, 3.6% d_5; 96.4% d_6; contact time for *m*-dinitrobenzene, 8.5 sec, and, for *o*- and *p*-dinitrobenzenes, 5 sec; N_2 at 10 cc/min. [b] Estimated from low-voltage (7.5 ionizing V nominal) mass spectrum. [c] Relative intensity of molecular ions summed for each chemical species in the low-voltage spectrum, normalized to total 100%. Some minor components are omitted from the listing, making the total intensities in the table <100%. [d] Contains some contribution from diphenylamines with one deuterium atom more.

phenyl radical derived solely from benzene, rather than from dinitrobenzene.

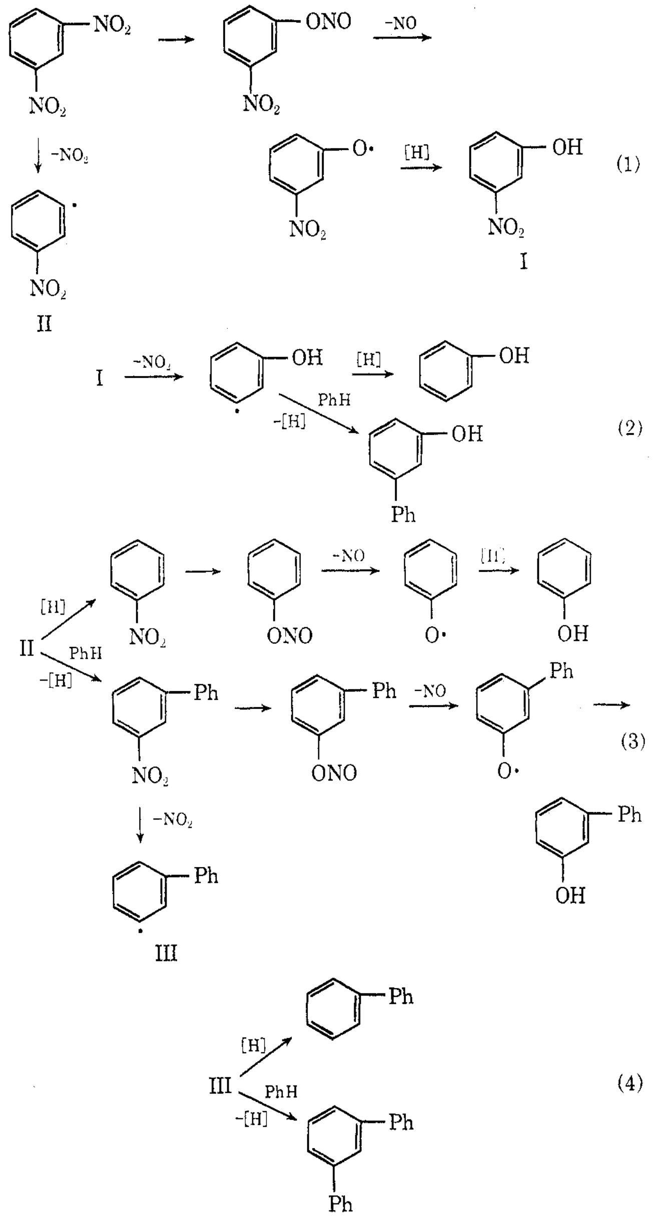
Thermal decomposition of *m*-dinitrobenzene seems to involve a series of consecutive steps that parallel in many ways its decomposition in the mass spectrometer. Loss of NO_2 gives nitrophenyl radical (II), which arylates benzene to nitrobiphenyl or abstracts hydrogen to form nitrobenzene. Nitrobiphenyl in turn loses NO_2; the biphenylyl radical (III) arylates benzene or abstracts hydrogen to form terphenyl and biphenyl, respectively. The latter reaction is minor, however, for almost all the biphenyl in the labeled run was biphenyl-d_{10}, derived solely from the benzene-d_6, by reaction 5. About 25% of the terphenyl was formed entirely from benzene-d_6, by way of phenyl-d_5 radicals from reaction of NO_2 with C_6D_6 (eq 5).

A minor identified product (0.9% of biphenyl) of mol wt 120 from the thermal reaction of *o*-dinitrobenzene and benzene, but not of the other isomers, proved to be the counterpart of the ion of this mass in the spectrum of *o*-dinitrobenzene by comparison with an authentic



SCHEME III

REACTIONS OF *m*-DINITROBENZENE WITH BENZENE



$$\mathrm{PhH} + \mathrm{NO_2} \xrightarrow{-\mathrm{HNO_2}} \mathrm{Ph\cdot} \xrightarrow[-[\mathrm{H}]]{\mathrm{PhH}} \mathrm{PhPh} \xrightarrow[[\mathrm{H}]]{\mathrm{Ph\cdot}} \mathrm{PhC_6H_4Ph} \quad (5)$$

sample. Formation of benzofurazan (2,1,3-benzoxadiazole) seems plausible and, as noted earlier, has precedents in thermal reactions of related materials.

Naphthalene was formed in ~1% yield in the reactions of all three dinitrobenzenes with benzene (Table I). The meta isomer with benzene-d_6 (Table III) gave only naphthalene-d_8, derived solely from benzene. At 650°, *o*-dinitrobenzene gave naphthalene with four to eight deuterium atoms; the para isomer gave only naphthalene-d_8. Total concentrations of naphthalene were, for *p*-dinitrobenzene, about the same as for the meta isomer at 500° and, for *o*-dinitrobenzene, three to four times as much. In spite of the thermal scrambling, the greater amount of naphthalene and its isotopic composition support the formation of benzyne as a minor path in the decomposition of *o*-dinitrobenzene at 650°.

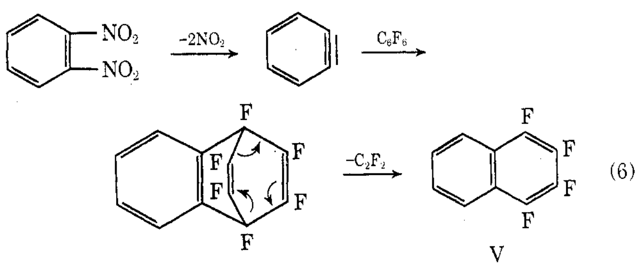
Additional evidence for benzyne from *o*-dinitrobenzene is shown in Table IV, which lists the products from the reactions of *o*- and *m*-dinitrobenzenes with hexafluorobenzene under identical conditions. Tetrafluoronaphthalene was formed only from the ortho isomer, presumably by reaction 6.

TABLE IV

REACTIONS OF *o*- AND *m*-DINITROBENZENES WITH HEXAFLUOROBENZENE[a]

Products	Relative concentrations[b] Ortho, 1.05[c]	Meta, 2.35[c]
Recovered reactants		
Dinitrobenzene	3.6	2.6
Hexafluorobenzene	33.9	9.3
Benzene	0.3	6.7
Pentafluorophenol	3.3	5.2
Tetrafluoronaphthalene	3.7	
Pentafluorobiphenyl	1.0	
Hexafluorobiphenyl	10.2	13.0
Heptafluorobiphenyl		2.6
Decafluorobiphenyl	1.1	2.6
Decafluoroterphenyl	0.8	29.0
Undecafluoroterphenyl		5.2
Other products, mostly unidentified[d]	42.1	23.8

[a] Conditions: 0.01 mol of dinitrobenzene, 0.5 mol of hexafluorobenzene; 650°; 10-sec contact time; N_2 at 10 cc/min. [b] Per cent of total ions in the low-voltage spectra (9.5 ionizing V nominal for products from the ortho products; 7.5 V from the meta). [c] Total weight of products, grams. [d] In both cases, the spectra gave evidence for a large number of products at low concentrations. Some of the observed peaks may be due to fragment ions arising from low-energy processes.



V (6)

The formation of naphthalene derivatives in the reactions of *o*-dinitrobenzene with benzene-d_6 and hexafluorobenzene is most readily explained by concerted or fast sequential loss of $2NO_2$ to give benzyne.

To find how the product distributions vary with other substituted benzenes and similar reagents, we allowed *m*-dinitrobenzene to react with fluoro- and chlorobenzenes, benzonitrile, pyridine, and thiophene. The products are listed in Table V.

Reactions of *m*- and *p*-dinitrobenzenes, as well as most reactions of *o*-dinitrobenzene, can be explained in terms of initial decomposition to NO_2 and nitrophenyl radical, paralleling primary loss of NO_2 in the mass spectra. To some extent, the nitrophenyl radical in turn loses NO_2 and gives products formally derived from phenylene diradical, although the actual intermediacy of such a diradical remains in doubt. The identification of benzofurazan both in the mass spectrum and among thermal reaction products of *o*-dinitrobenzene points to an alternative and unexpected interaction between the nitro groups in this isomer.

TABLE V

REACTIONS OF *m*-DINITROBENZENE[a]

Products	Relative concentrations[b] Fluorobenzene (R = C_6H_4F), 2.2[c]	 Chlorobenzene (R = C_6H_4Cl), 2.75[c]	 Benzonitrile (R = C_6H_4CN), 2.5[c]	 Pyridine (R = C_5H_4N), 2.3[c]	 Thiophene (R = C_4H_3S), 1.15[c]
Phenol	8			5	9
ROH	13	6	18	13	
RC_6H_5	46	26	99	36	116
RC_6H_4OH	11		13	15	67
RR	100	100	100	100	100
$RC_6H_4NO_2$	9	24	10	11	22
RC_6H_4R	21	13	36	37	110

[a] Conditions: 0.01 mol of *m*-dinitrobenzene, 0.1 mol of reagent; 550°; 15-sec contact time; N_2 at 10 cc/min. [b] Relative intensities in the low-voltage mass spectrum normalized to RR = 100. [c] Total weight of products, grams.

Registry No.—*o*-Dinitrobenzene, 528-29-0; *m*-dinitrobenzene, 99-65-0; *p*-dinitrobenzene, 100-25-4; benzene, 71-43-2; hexafluorobenzene, 392-56-3.

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Ring Strain Effects. V.[1] An Electron Spin Resonance Study of the Anion Radicals of a Series of O-Disubstituted Benzenes

STEPHEN E. BALES[2] AND REUBEN D. RIEKE*

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514

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The effects of ring strain on spin densities of aromatic radical anions has been investigated for a series of substituted benzene derivatives. The spin density was found to increase at the positions α to the ring juncture carbons containing the fused strained ring. The results are described in terms of a hybridization-polarization mechanism. Also, ion-pairing effects on spin densities are discussed.

The effects of a strained fused ring on the chemical and physical properties of aromatic hydrocarbons has been the subject of much research. Numerous reports have appeared concerning the increased preference for electrophilic attack β to the fused ring as strain is increased.[3-9] Markgraf has reported on the changes in the basicity of the lone pair of electrons of a nitrogen α to a fused ring.[10] Also, it has been reported that the acidity of protons α to the fused ring increases as the ring strain is increased.[11,12] An orbital hybridization-polarization model has been put forth which is in accord with these observations.[11,12] Several different types of physical and chemical properties have been interpreted within this model: nmr data,[13,14] epr data,[1,15] rates of protodesilylation,[16] polarographic reduction potentials,[17] molecular orbital calculations,[18] and ir data.[19]

In this paper, we would like to report the epr spectra of a series of benzene derivatives with varying amounts of strain in the fused rings. The results are discussed in terms of the hybridization-polarization model. Effects of ion-pairing on spin densities are also examined. The compounds examined and the numbering system used are shown in Chart I. Hyperfine splitting constants (hfsc) are given in gauss throughout the text.

Experimental Section

The general techniques and procedures employed for preparing the radical anions in this study have been discussed previously.[15d]

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