

not predictable with any accuracy by a simple model or comparison.

**Acknowledgment.**—This work was supported by Haverford College faculty research funds.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, AMERICAN OIL CO., WHITING, IND.]

## Organic Ions in the Gas Phase. XII. Aniline

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RECEIVED MAY 2, 1963

Several of the ionization-dissociation processes of aniline under electron impact have been deduced from the mass spectra of anilines unlabeled and labeled in three ways: *-3-d*, *-2,4,6-d<sub>3</sub>*, and *-N<sup>15</sup>*. The major primary process involves loss of HCN; minor competing processes involve loss of H, CH<sub>3</sub>, NH<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, and C<sub>2</sub>H<sub>3</sub>. The nitrogen atom clearly plays a central role in determining the course of reaction of the aniline ion.

Although aniline bears a structural resemblance to toluene, the mass spectra of the two compounds<sup>3</sup> differ markedly. The parent ion is by far the most abundant ion in the spectrum of aniline. The most abundant ion in that of toluene is formed by loss of a hydrogen atom; the corresponding product in the aniline spectrum is a distinctly minor one. The most abundant fragment ion from aniline is that of mass 66, formed apparently by loss of HCN from the parent ion; analogous loss of C<sub>2</sub>H<sub>2</sub> from toluene is barely perceptible. The sharp differences found between the gross behavior of aniline and toluene prompted a closer examination of the former.

Spectra of labeled species of other compounds have helped clarify many ionization-dissociation processes induced by electron impact.<sup>4</sup> An earlier study of the aniline spectrum<sup>5</sup> was handicapped by the mass equivalence of a nitrogen atom and a methylene group; much of this difficulty can be removed by labeling with N<sup>15</sup>. We have therefore studied the mass spectra of aniline unlabeled, *-3-d*, *-2,4,6-d<sub>3</sub>*, and *-N<sup>15</sup>*. The general procedure followed in interpreting the spectra of labeled compounds has been described elsewhere.<sup>4</sup>

### Experimental

Aniline-*-3-d* and *-N<sup>15</sup>* were available from an earlier study.<sup>6</sup> We are indebted to John G. Burr, Jr., of North American Aviation, for the gift of a sample of aniline-*-2,4,6-d<sub>3</sub>*.<sup>7</sup> Unlabeled aniline was redistilled commercial material. Isotopic composition of the labeled species was determined by mass spectrometry at reduced ionizing voltage<sup>8</sup>: aniline-*-3-d*, 95.8%; aniline-*-2,4,6-d<sub>3</sub>*, 96.8% (*-d<sub>0</sub>*, 0.2%; *-d<sub>2</sub>*, 2.5%; *-d<sub>4</sub>*, 0.5%); and aniline-*-N<sup>15</sup>*, 31.9%.

Spectra were measured with 70 e.v. on a Consolidated model 21-103c instrument. Partial spectra, shown in Table I, have been corrected for unlabeled aniline in the labeled materials and for naturally occurring heavy isotopes. For peaks in the parent-mass region, the latter correction was based on the known natural abundance of C<sup>13</sup> and N<sup>15</sup>. For all other peaks, the possible presence of nitrogen was disregarded, and an approximate correction was made using factors derived for hydrocarbon ions of the same masses.<sup>9</sup> The complete spectra will be submitted for publication elsewhere.<sup>3</sup>

The spectrum obtained for unlabeled aniline is closely similar to a previously published one<sup>5</sup> except that it contains a normal peak at mass 78 and metastable peaks at 91.1, 64.1, and 46.8, none of which was reported in the earlier work.

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### Decomposition Reactions

At least seven decomposition reactions can be deduced from the spectra

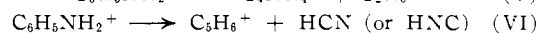
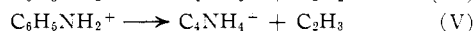
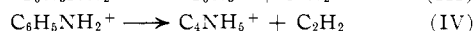
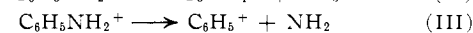
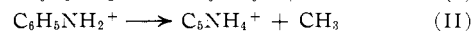


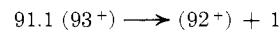
TABLE I

<i>m/e</i>	PARTIAL MASS SPECTRA OF ANILINES			
	Unlabeled	<i>-3d</i>	<i>-2,4,6-d<sub>3</sub></i> <sup>a</sup>	<i>-N<sup>15</sup></i>
65	18.4	4.66	3.57	17.0
66	32.4	17.6	3.41	32.8
67	3.21	31.6	6.23	2.5
68	..	2.07	17.4	3.0
69	..	..	28.7	0.1
70	..	..	0.61	..
76	1.22	0.61	.64	1.2
77	1.17	0.96	.43	1.4
78	1.94	1.95	.71	0.0
79	..	1.06	1.13	2.0
80	..	..	2.03	..
81	..	..	0.19	..
91	1.05	0.35	.12	0.0
92	10.8	1.13	.17	0.9
93	100.0	10.2	.0	11.7
94	..	100.0	1.85	100.0
95	..	..	11.8	..
96	..	..	100.0	..
97	..	..	0.3	..

<sup>a</sup> Uncorrected for 2.5% *-d<sub>2</sub>* and 0.5% *-d<sub>4</sub>*.

Independent supporting evidence for reactions I, VI, and VII is provided by metastable peaks.<sup>4,10</sup>

**I. C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub><sup>+</sup> → C<sub>6</sub>NH<sub>6</sub><sup>+</sup> + H.**—This reaction is the source of the normal peaks of parent mass less one and of the metastable peaks



in the spectra of aniline unlabeled, *-3-d*, and *-2,4,6-d<sub>3</sub>*, respectively. The source of the hydrogen atom is not completely defined, because even small uncertainties in the isotopic analyses would result in proportionately large errors at the parent mass less one. Nonetheless, most of the hydrogen lost is evidently protium in all the spectra and therefore comes from the amino group. Similarly, the C<sub>6</sub>NH<sub>5</sub><sup>+</sup> ion evidently arises by loss of H<sub>2</sub> or 2H chiefly from the amino group.

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II.  $C_6H_5NH_2^+ \rightarrow C_5NH_4^+ + CH_3$ .—Relative intensity of unlabeled aniline at mass 78 is nearly identical with that of aniline- $N^{15}$  at 79. Thus, the ions producing these peaks all retain the nitrogen atom and are formed by loss of  $CH_3$ . Retention of deuterium in  $C_5NH_4^+$  from aniline-3- $d$  (obtained from the intensity at mass 79) and of all three deuterium atoms in this ion from aniline-2,4,6- $d_3$  (obtained from the intensity at mass 81) agree closely with values predicted for random loss of three out of seven hydrogens.

	Observed	Predicted
3- $d$ , %	55	57
2,4,6- $d_3$ , %	10	11

Such loss of positional identity suggests a randomizing sequence of rearrangements, possibly involving an intermediate of higher symmetry than the original aniline ion.

The complete isotopic distribution of the  $C_5NH_4^+$  ions calculated for such a randomizing process in the  $d_3$ -species is:  $-d_3$ , 11%;  $-d_2$ , 52%;  $-d_1$ , 34%; and  $-d_0$ , 3%. These ions would contribute 1.01 units to the relative intensity at mass 80, 0.66 at 79, and 0.06 at 78. The contribution of unlabeled  $C_5NH_4^+$  at 78 in the spectrum of aniline-3- $d$  is estimated at 1.94 – 1.06 or 0.88 unit.

III.  $C_6H_5NH_2^+ \rightarrow C_6H_5^+ + NH_2$ .—Relative intensity of unlabeled aniline at mass 77, 1.17, is taken as a measure of total  $C_6H_5^+$  yield in all isotopic species. Possible interference from a  $C_5NH_3^+$  ion, which would have the same mass, is ruled out by the absence of a detectable peak at mass 78 in the aniline- $N^{15}$  spectrum. In the spectrum of aniline-3- $d$ , the yield of  $C_6H_4D^+$  is given by the intensity at mass 78 after subtracting that portion attributed to unlabeled  $C_5NH_4^+$ :  $1.95 - 0.88 = 1.07$ . Nearly all the *meta* deuterium is thus retained in the  $C_6H_5^+$  ion; not more than 10% is lost in the amino radical. The aniline-2,4,6- $d_3$  data are interpreted similarly. The contribution of  $C_5NH_2D_2^+$  at mass 80 is 1.01 units. The remainder of the intensity at 80,  $2.03 - 1.01$  or 1.02 units, is attributed to  $C_6H_2D_3^+$ ; 88% of the  $C_6H_5^+$  ions appear to retain all three deuterium atoms. Thus, simple cleavage of the  $C_6H_5-NH_2$  bond comes close to accounting for the observed label retentions.

IV.  $C_6H_5NH_2^+ \rightarrow C_4NH_5^+ + C_2H_2$ .—Relative intensity of aniline- $N^{15}$  at mass 68, 3.0, is close enough to that of unlabeled aniline at 67, 3.21, to suggest that no nitrogen is lost in forming the latter ion and that the reaction occurring is correctly represented by eq. IV. Intensity of aniline-3- $d$  at 68 shows that  $2.07/3.21$  or 64% of the product ions retain the *meta* deuterium. Intensity of aniline-2,4,6- $d_3$  at 70 shows that  $0.61/3.21$  or 19% of the product ions retain all three deuterium atoms. These statistics agree closely with retentions predicted for random loss of two out of six hydrogens, the five from the ring and one from the amino group, but not for random loss of two out of the original five from the ring alone or out of seven.

	Observed	Predicted for random loss of 2 out of 6		
		6	5	7
3- $d$ , %	64	67	60	71
2,4,6- $d_3$ , %	19	20	10	29

The complete isotopic distribution of the  $C_4NH_5^+$  ions calculated for such a randomizing process in aniline- $d_3$  is:  $-d_3$ , 20%;  $-d_2$ , 60%;  $-d_1$ , 20%; and  $-d_0$ , none. These ions would contribute 1.92 units to relative intensity at 69 and 0.64 at 68. The  $C_4NH_5^+$  contribution at 67 in the spectrum of aniline-3- $d$  is estimated at  $3.21 - 2.07$  or 1.14 units.

V.  $C_6H_5NH_2^+ \rightarrow C_4NH_4^+ + C_2H_3$ .—The aniline- $N^{15}$  peak at mass 67 implies that the nitrogen atom is retained in 2.5/32.4 or 8% of the mass-66 ions derived from unlabeled aniline. The  $C_4NH_4^+$  ion so indicated may be formed from the parent ion by reaction V or, alternatively, it may be formed from  $C_6NH_6^+$  by loss of  $C_2H_2$  or from  $C_4NH_5^+$  by loss of H. The available evidence does not permit a choice.

VI.  $C_6H_5NH_2^+ \rightarrow C_5H_6^+ + HCN$  (or HNC).—This reaction is supported by the metastable peaks

46.8 (93 <sup>+</sup> )	→	(66 <sup>+</sup> ) + 27
47.8 (94 <sup>+</sup> )	→	(67 <sup>+</sup> ) + 27
49.6 (96 <sup>+</sup> )	→	(69 <sup>+</sup> ) + 27

in the spectra of aniline unlabeled, -3- $d$ , and -2,4,6- $d_3$ , respectively. The spectrum of the aniline- $N^{15}$  sample contains a diffuse peak in the region of mass 46 to 47, the shape of which suggests that it consists of two overlapping metastable peaks. These are presumably

46.3 (94 <sup>+</sup> )	→	(66 <sup>+</sup> ) + 28
46.8 (93 <sup>+</sup> )	→	(66 <sup>+</sup> ) + 27

The former corresponds to reaction VI of aniline- $N^{15}$ . The latter is attributed to unlabeled aniline, which comprised 68% of the sample.

Total yield of  $C_5H_6^+$  is given by the intensity of unlabeled aniline at mass 66 less the intensity attributed to  $C_4NH_4^+$ :  $32.4 - 2.5$  or 29.9 units. In the spectrum of aniline-3- $d$ ,  $C_4NH_5^+$  accounts for 1.14 units of intensity at 67. The remainder,  $31.6 - 1.14$  or 30.5 units, includes  $C_4NH_3D^+$  and  $C_5H_5D^+$ . The intensity attributable to  $C_5H_5D^+$  is 28.0 to 30.5, depending on how much  $C_4NH_4^+$  is labeled; the label is thus retained in 94 to 102% of the product ions. In the spectrum of aniline-2,4,6- $d_3$ , the estimated yield of  $C_4NH_3D_2^+$  accounts for 1.92 units at 69. The remainder of the intensity at 69,  $28.7 - 1.92$  or 26.8 units, includes both  $C_4NHD_3^+$  and  $C_5H_3D_3^+$ . The intensity attributable to  $C_5H_3D_3^+$  is 24.3 to 26.8, depending on how much  $C_4NH_4^+$  is triply labeled; all three deuterium atoms are thus retained in 81 to 90% of the product ions.

If the HCN hydrogen comes from any of the five ring positions with equal probability, a loss of 6% of the label in forming the  $C_5H_6^+$  ion from the  $d_1$ -species would mean that  $5 \times 6\%$ , or 30%, of the HCN hydrogen comes from the ring. Similarly, a loss of deuterium in 19% of the aniline- $d_3$  decompositions would mean that  $5/3 \times 19\%$ , or 32%, of the hydrogen comes from the ring. Although most of the HCN hydrogen clearly originates in the amino group, part of it, possibly as much as 32%, comes from the ring.

VII.  $C_5H_6^+ \rightarrow C_5H_5^+ + H$ .—This reaction is supported by the metastable peaks

64.1 (66 <sup>+</sup> )	→	(65 <sup>+</sup> ) + 1
65.1 (67 <sup>+</sup> )	→	(66 <sup>+</sup> ) + 1
67.1 (69 <sup>+</sup> )	→	(68 <sup>+</sup> ) + 1
64.1 (66 <sup>+</sup> )	→	(65 <sup>+</sup> ) + 1

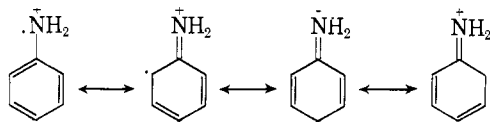
in the spectra of aniline unlabeled, -3- $d$ , -2,4,6- $d_3$ , and - $N^{15}$ , respectively. The  $C_5H_5^+$  ion is derived at least in part from a  $C_5H_6^+$  precursor.

Relative intensity of aniline- $N^{15}$  at mass 66 is greater than can be accounted for by  $C_5H_6^+$ . The excess,  $32.8 - 29.9$  or 2.9 units, is attributed to  $C_4N^{15}H_3^+$ . Therefore, in unlabeled aniline,  $2.9/18.4$  or 16% of the observed intensity at 65 is attributed to  $C_4NH_3^+$ ;  $C_5H_5^+$  contributes the remaining 84%.

### Discussion

The parent ion of aniline is apparently a highly stable species. It accounts for 59% of total ion intensity in the mass spectrum; the corresponding figure for toluene

is only 24%. This finding is in keeping with other evidence for high stability, in a rather different environment. When the aniline ion is formed by photoionization in a hydrocarbon glass at low temperature, it survives long enough to be detected spectroscopically.<sup>11</sup> An explanation may lie in resonance stabilization predicted for a molecule that has lost a nonbonding electron—similar to that proposed for Wurster's salt<sup>12</sup>



and as an intermediate in induced decomposition of acyl peroxides by amines.<sup>13</sup> These structures offer a further possible clue to understanding the spectrum of aniline. In the toluene ion, the charge in the  $\pi$ -electron system is thought to furnish the driving force for ring expansion.<sup>4</sup> If so, localization of the charge on the nitrogen atom in the aniline ion might be expected to favor rather different reaction paths.

The principal decomposition path is by reaction VI. Marked preference for the path is doubtless promoted by the high stability of HCN, which seems to be a favored product from many reactive systems containing the necessary elements even though its formation may require extensive rearrangement. Thus, ions formed by loss of HCN are prominent in the mass spectra not only of aniline, but also, for example, of dinaphthylamine,<sup>14</sup> benzonitrile,<sup>14</sup> phthalonitrile,<sup>15</sup>  $\alpha$ -picoline,<sup>15</sup> nicotinonitrile,<sup>15</sup> phthalimide,<sup>15</sup> and 4-carboxyphthalimide.<sup>15</sup> Attention has been drawn to the close parallel between loss of HCN from nitrogen-containing compounds and the well known, highly favored loss of CO in many classes of oxygen-containing com-

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pounds.<sup>14</sup> In other contexts, HCN has been reported to be the main product of the reactions between active nitrogen and a variety of hydrocarbons and hydrocarbon derivatives.<sup>16</sup> It has been found among the products formed by passing a spark discharge through a mixture of nitrogen and formic acid.<sup>17</sup> It is also formed in reactions of methyl radicals with nitric oxide<sup>18</sup> and of hydrogen atoms with methyl-, dimethyl-, trimethyl-, and ethylamines.<sup>19</sup>

The toluene ion rearranges to a seven-membered ring and loses hydrogen to give the stable tropylium ion.<sup>4, 20</sup> Further decomposition occurs largely from this primary product. In contrast, the aniline ion seems to have no strong tendency to lose hydrogen. When it does so, loss occurs chiefly from the amino group, and side-chain and ring hydrogen atoms do not lose identity, as they do in toluene. Nevertheless, rearrangements are involved in most of the processes by which the aniline ion decomposes. In reaction II, all seven hydrogen atoms apparently lose identity; in reaction IV, the five ring hydrogens and one of the two amino hydrogens seem to be scrambled. Even in these two processes, the asymmetry introduced by the nitrogen atom makes a proposal of ring expansion less attractive in aniline than in toluene. Further labeling, especially with C<sup>13</sup>, might help resolve the uncertainty as to whether ring expansion plays any part in the chemistry of aniline under electron impact.

Detailed examination of the mass spectrum of aniline and, especially, the pronounced differences between aniline and toluene emphasize the central role of the nitrogen atom in determining the course of reaction of the aniline ion.

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{CONTRIBUTION FROM THE GORGAS LABORATORY, ROHM & HAAS COMPANY, REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALA.}

## Nitrosohydroborates. I

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RECEIVED APRIL 17, 1963

The first nitrosohydroborate,  $B_{20}H_{18}NO(NHET_3)_3$ , was prepared by the reaction of bistriethylammonium decahydrodecaborate,  $B_{10}H_{10}(NHET_3)_2$ , with nitrogen dioxide or ferric ion and nitric oxide. The nitroso group was readily reduced to the amino derivative producing  $B_{20}H_{18}NH_2^{-3}$ . Halogenation led to  $B_{20}H_{10}F_8NO^{-3}$ ,  $B_{20}H_2Cl_{16}NO^{-3}$ ,  $B_{20}H_4Br_{14}NO^{-3}$ , and  $B_{20}H_{11}I_7NO^{-3}$ . On reduction the corresponding halogenated amino compounds were obtained. They could be reoxidized to the original nitrosoborates. Various physical properties such as infrared, visible, and B<sup>11</sup> n.m.r. spectra for the compounds are presented.

### Introduction

Among the numerous derivatives of boranes and hydroborate ions known there are no compounds reported to date containing an NO group directly attached to one of the boron atoms. One might expect low stability from such a compound and thus only the most stable boranes or borane ions might be capable of forming a stable nitroso derivative. It was therefore interesting to note that the oxidation of decahydrodecaborate salts<sup>1,2</sup> with mild oxidants such as ferric nitrate was accompanied by the appearance of an intense blue color. The fact that the latter did not de-

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(2) W. N. Lipscomb, A. R. Pitochelli, and M. F. Hawthorne, *ibid.*, **81**, 5833 (1959).

velop when ferric sulfate or ferric chloride was employed suggested the presence of a nitroso or nitro compound. It was found that ferric ion in combination with nitric oxide or nitrite ion as well as alkyl nitrite and concentrated nitric acid would also produce the same intense color. Extension of this reaction to other boranes, *i.e.*, decaborane and bisacetone-triledecaborane, did not lead to interesting products. Decaborane was oxidized to boric acid and bisacetone-triledecaborane produced an unstable, intractable green oil.

### Results and Discussion

**A. The Preparation of  $B_{20}H_{18}NO(NHET_3)_3$ .**—The reaction of decahydrodecaborate ion with ferric ion-nitric oxide essentially parallels that with nitrogen dioxide so that the discussion can be restricted to the