693. *Pyrolyses of* NN-*Dimethylaniline, Cumene, and Phenylhydrazine, and Bond Strengths in Aromatic Amino-compounds.*

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Pyrolyses of *NN*-dimethylaniline, cumene, and phenylhydrazine have been studied by the aniline-carrier technique and found to be first-order homogeneous reactions with the following rate constants: *NN*-dimethylaniline (552—681°) $\log k$ (sec.$^{-1}$) $= 12{\cdot}9 - (57{,}000/2{\cdot}3\boldsymbol{R}T)$; cumene (619—716°) $\log k = 14{\cdot}3 - (66{,}000/2{\cdot}3\boldsymbol{R}T)$; phenylhydrazine (325—437°) $\log k = 11{\cdot}8 - (40{,}000/2{\cdot}3\boldsymbol{R}T)$. From the first two values it is deduced that methyl substitution has about the same weakening effect on N–C and N–H bond strengths in anilines as on the corresponding C–C and C–H bonds in alkylbenzenes. The heat of formation of the amino-radical derived from the pyrolysis of phenylhydrazine agrees with a revised figure [$\Delta H_f°(NH_2) = 39{\cdot}3$ kcal. mole^{-1}] from the pyrolysis of hydrazine.

IT has recently been shown [1,2] that replacement of toluene by aniline in a toluene-carrier experiment leads to more reliable kinetic data on the pyrolyses of compounds which break up to yield a methyl radical. This Paper reports an extension of the technique to study the effect of methyl substitution on C–N bond strengths in anilines. To compare this effect with the analogous C–C bond strengths it was necessary to re-investigate the pyrolysis of cumene. Finally, the pyrolysis of phenylhydrazine has also been studied to extend our information on N–N bond dissociation energies, several of which have been reported from toluene-carrier experiments.[3]

EXPERIMENTAL

Apparatus and Procedure.—The experiments were identical with those previously described.[1,2] Injections of reactants were made by evaporating aniline solutions of predetermined composition. Analyses of the product mixtures, of hydrogen and methane,[1] or nitrogen and ammonia,[3] have also been described.

Materials.—The compounds pyrolysed were commercial samples; they were distilled twice and constant-boiling fractions collected.

RESULTS AND DISCUSSION

The Pyrolysis of NN-*Dimethylaniline.*—Results, presented in Table 1, were obtained over the temperature range 552—681°, with contact times from 0·6 to 2·3 sec. and total pressures from 6 to 12 mm. of Hg. The only gaseous products were methane and hydrogen, which can be accounted for by the following mechanism:

$$PhN(CH_3)_2 = Ph\dot{N}{\cdot}CH_3 + CH_3{\cdot} \qquad (1)$$

$$CH_3{\cdot} + PhNH_2 = CH_4 + PhNH{\cdot} \qquad (2)$$

$$2PhNH{\cdot} = (PhNH)_2 \qquad (3)$$

$$PhNH_2 = PhNH{\cdot} + H{\cdot} \qquad (4)$$

$$H{\cdot} + PhNH_2 = H_2 + PhNH{\cdot} \qquad (5)$$

This mechanism is in accord with previous findings,[1,2] that the anilino-radicals appear to dimerise and that the formation of hydrogen from aniline is analogous to that from toluene. It follows that rate constants for the unimolecular decomposition of dimethylaniline can be calculated in the normal manner from the yields of methane. As may be deduced from Table 1, these rate constants are independent of contact-time, pressure, and the ratio of surface to volume of the reaction vessel. A least-mean-squares treatment gives:

$$\log k_1\ (\text{sec.}^{-1}) = (12{\cdot}9 \pm 0{\cdot}15) - (57{,}031 \pm 600/2{\cdot}3\boldsymbol{R}T).$$

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[1] Esteban, Kerr, and Trotman-Dickenson, *J.*, 1963, 3873.
[2] Esteban, Kerr, and Trotman-Dickenson, *J.*, 1963, 3879.
[3] Kerr, Sekhar, and Trotman-Dickenson, *J.*, 1963, 3217.

The Pyrolysis of Cumene.—The pyrolyses of alkylbenzenes by the toluene-carrier technique were first investigated by Szwarc and his co-workers.[4-6] Re-investigation of the pyrolyses of ethyl-, n-propyl-, and n-butyl-benzene by the aniline-carrier technique has, however, led to revised activation energies for these decompositions. It was, therefore, thought that the pyrolysis of cumene, also previously studied by Szwarc and of interest in comparison with dimethylaniline, should be re-investigated by the new technique.

TABLE 1.

The pyrolysis of *NN*-dimethylaniline.

Temp. (°K)	Total pressure (mm.)	Contact time (sec.)	$PhN(CH_3)_2$ (10^{-5} mole)	H_2 (10^{-5} mole)	CH_4 (10^{-5} mole)	10^2k_1 (sec.$^{-1}$)
825·5	7·0	0·76	78·5	0·062	0·481	0·76
835·8	7·2	0·77	80·4	0·128	0·586	0·87
840·5	7·1	0·75	72·0	0·193	0·642	1·21
846·1	7·1	0·73	75·3	0·137	0·663	1·16
847·5	7·0	0·75	59·6	0·136	0·655	1·43
851·5	9·2	1·25	77·0	0·242	1·88	1·99
852·0	7·1	0·76	60·2	0·179	0·675	1·43
852·5 *	12·3	2·26	59·6	0·143	2·62	2·01
861·0	7·2	0·67	79·8	0·162	1·61	2·94
872·5	5·8	0·61	41·3	0·197	0·985	3·89
873·0 *	9·1	1·29	34·0	0·201	1·50	3·47
873·5	12·4	2·27	44·6	0·511	4·20	4·37
873·7	6·0	0·62	84·7	0·183	2·15	4·17
874·0	7·0	0·70	55·9	0·244	1·94	5·03
884·0	7·2	0·71	55·2	0·229	1·81	4·71
888·5	6·8	0·70	83·7	1·28	6·23	11·0
905·0	7·1	0·67	50·8	0·720	3·92	12·1
918·5	7·1	0·69	28·0	0·431	4·47	25·2
936·0	7·3	0·76	47·5	2·41	11·8	37·6
937·2	6·0	0·77	67·3	3·02	14·5	31·5
937·6	5·9	0·63	56·8	2·72	11·4	35·6
939·0	5·3	0·66	27·7	1·39	6·52	40·7
942·1	5·6	0·54	39·4	1·74	7·61	39·6
942·1	5·8	0·58	34·4	1·84	7·47	42·4
951·9	5·1	0·52	28·8	2·23	10·1	83·3
953·2	5·6	0·52	44·6	3·51	13·1	66·6
954·1	6·3	0·54	109·6 *	8·91	36·1	71·1

* Packed vessel.

Runs were carried out over the temperature range 619—716° with a contact time of about 0·7 sec. and a total pressure of about 7 mm. of Hg. Variation of contact-time, total pressure, and surface to volume ratio of reaction vessel had been shown by Szwarc to have no effect on the first-order rate constants. Again the gaseous products were hydrogen and methane, and hence the mechanism will be similar to that proposed by Szwarc, namely,

$$\mathrm{PhCH(CH_3)_2 = Ph\dot{C}H{\cdot}CH_3 + CH_3{\cdot}} \qquad (6)$$

$$\mathrm{CH_3{\cdot} + PhNH_2 = CH_4 + PhNH{\cdot}} \qquad (2)$$

$$\mathrm{2PhNH{\cdot} = (PhNH)_2} \qquad (3)$$

In addition to the small amounts of hydrogen produced from the decomposition of aniline [reactions (4) and (5)], hydrogen is also thought to result from the decomposition of the radical $\mathrm{PhCH{\cdot}CH_3}$:

$$\mathrm{Ph\dot{C}H{\cdot}CH_3 = PhCH{:}CH_2 + H{\cdot}} \qquad (7)$$

$$\mathrm{H{\cdot} + PhNH_2 = H_2 + PhNH{\cdot}} \qquad (8)$$

First-order rate constants for reaction (6), calculated from the methane as before, are given in Table 2 which also summarises the other experimental data. Least-mean-squares treatment gives,

$$\log k_6\ (\text{sec.}^{-1}) = (14{\cdot}3 \pm 0{\cdot}2) - (66{,}000 \pm 800/2{\cdot}3\boldsymbol{R}T).$$

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[4] Szwarc, *J. Chem. Phys.*, 1949, **17**, 431.

[5] Leigh and Szwarc, *J. Chem. Phys.*, 1952, **20**, 403.

[6] Leigh and Szwarc, *J. Chem. Phys.*, 1952, **20**, 844.

Leigh and Szwarc [6] favoured

$$\log k_6 \text{ (sec.}^{-1}) = 13{\cdot}3 - (61{,}000/2{\cdot}3\boldsymbol{R}T),$$

but the plot of points shows distinct curvature. The rate constants at the extremes of the temperature scale agree reasonably well with ours but are significantly higher in the middle of the range. Recognizing the difficulty of drawing the correct line through their points, Leigh and Szwarc based their value of the activation energy on the assumption that the *A*-factor for cumene was twice that found previously for ethylbenzene. This relation does not hold as the *A*-factor for the ethylbenzene decomposition has recently been shown [1] to be $10^{14{\cdot}6}$ sec.$^{-1}$.

TABLE 2.

The pyrolysis of cumene.

Temp. (°K)	Total pressure (mm.)	Contact time (sec.)	$PhCH(CH_3)_2$ (10^{-5} mole)	H_2 (10^{-5} mole)	CH_4 (10^{-5} mole)	10^2k_6 (sec.$^{-1}$)
892·5	7·0	0·83	71·1	0·749	0·896	1·47
906·0	7·6	0·75	49·7	0·743	0·937	2·51
913·1	7·1	0·70	85·8	1·70	1·92	3·25
914·0	7·7	0·74	64·3	1·40	1·62	3·23
927·1	7·5	0·77	55·8	2·09	2·40	5·70
941·7	7·9	0·76	41·7	2·76	3·02	9·76
948·0	7·4	0·74	45·2	3·97	4·19	13·2
957·5	7·2	0·70	29·1	2·67	3·09	20·6
957·5	7·4	0·72	48·6	5·28	5·37	16·1
979·5	7·1	0·69	36·6	6·71	7·70	34·4
980·2	7·3	0·71	39·9	9·56	9·42	38·0
989·0	7·4	0·70	32·6	9·28	10·4	54·8

Bond Strengths in Anilines.—By making the usual assumption that the activation energies of the unimolecular reactions correspond to the strengths of the bonds broken, it is possible to compare dissociation energies of N–C and N–H bonds in anilines with the corresponding C–C and C–H bonds in alkylbenzenes. Thus, methyl substitution in anilines appears to have about the same effect on the N–C and N–H bond strengths as on the corresponding C–C and C–H bonds in the hydrocarbons. This is in marked contrast to the effect found with C_6H_5–N bonds in anilines and N–C and N–H bonds in amines, where methyl substitution has a considerably greater weakening effect than on the corresponding bonds in hydrocarbons (Table 10 in ref. 3).

TABLE 3.

Dissociation energies of bonds in anilines.

Bond	*D* (kcal. mole^{-1})	Ref.	Radical	ΔH_f° (radical) (kcal. mole^{-1})	ΔH_f° (parent compound)	Ref.
PhNH–H	80·1	2	PhNH·	47·7	19·6	7
$PhN(CH_3)$–H	74·5 †	This work	$PhN{\cdot}CH_3$	44·1	21·6	‡
$PhCH_2$–H	84·6	1	$PhCH_2{\cdot}$	44·5	—	—
$PhCH(CH_3)$–H	78·0 †	This work	$PhCH{\cdot}CH_3$	33·0	—	—
PhNH–CH_3 *	60·0	2	—	—	—	—
$PhN(CH_3)$–CH_3 *	57·0	This work	—	—	20·1	§
$PhCH_2$–CH_3 *	70·1	1	—	—	—	—
$PhCH(CH_3)$–CH_3	66·0	This work	—	—	—	—

* $H_f^\circ(CH_3) = 33{\cdot}9$ kcal. mole^{-1} (Fettis and Trotman-Dickenson, *J.*, 1961, 3037). † Calculated from $D = \Delta H_f^\circ$ (radical) $+ \Delta H_f^\circ$ (H) $- \Delta H_f^\circ$ (parent compound). ‡ Garner and Abernathy, *Proc. Roy. Soc.*, 1921, *A*, **99**, 213; Klages, *Chem. Ber.*, 1949, **82**, 358. § Vriens and Hill, *Ind. Eng. Chem.*, 1952, **44**, 2732.

The Pyrolysis of Phenylhydrazine.—Table 4 lists the conditions and results of this

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[7] Anderson and Gilbert, *J. Amer. Chem. Soc.*, 1942, **64**, 2369.

reaction studied between 325 and 437°. The gaseous products consisted of nitrogen and ammonia. From previous work[3] the following mechanism is suggested for the homogeneous decomposition:

$$\mathrm{PhNH{\cdot}NH_2 = PhNH{\cdot} + NH_2{\cdot}} \tag{9}$$

$$\mathrm{NH_2{\cdot} + PhNH_2 = NH_3 + PhNH{\cdot}} \tag{10}$$

$$\mathrm{2PhNH{\cdot} = (PhNH)_2} \tag{3}$$

Nitrogen is presumably formed heterogeneously, but two runs with a packed reaction vessel showed that ammonia is not formed in this way. First-order rate constants (k_9) were calculated from the yields of ammonia and shown to be independent of contact time, percentage decomposition, and total pressure. An Arrhenius plot gives a good straight line, and a least-mean-squares calculation yields the equation:

TABLE 4.

The pyrolysis of phenylhydrazine.

Temp. (°K)	Total pressure (mm.)	Contact time (sec.)	$\mathrm{PhNH{\cdot}NH_2}$ (10^{-5} mole)	$\mathrm{NH_3}$ (10^{-5} mole)	$\mathrm{N_2}$ (10^{-5} mole)	10^2k_9 (sec.$^{-1}$)
607·7	11·6	3·27	30·0	0·297	0·363	0·320
613·2	12·8	3·46	28·9	0·541	0·364	0·452
619·5	12·4	3·08	37·0	0·667	0·155	0·634
624·4 *	12·1	3·34	43·1	0·959	0·354	0·683
627·7	9·4	1·92	34·4	0·557	0·341	0·914
628·4	9·0	1·81	30·7	0·457	0·217	0·833
628·5	12·1	3·12	52·9	1·24	0·200	0·853
629·3	12·0	3·07	42·2	0·929	0·195	0·714
633·5	9·1	1·90	60·3	1·18	0·280	1·15
634·8	8·8	1·69	39·4	0·752	0·119	1·91
635·5	6·1	1·03	37·4	0·523	0·217	1·35
637·4	9·3	1·76	17·9	0·437	0·125	1·38
638·0	12·8	3·28	34·6	1·68	0·283	1·51
638·0 *	11·8	3·51	36·9	1·55	0·832	1·23
641·2	9·4	1·85	63·4	1·10	0·271	2·38
645·1	9·1	1·803	50·9	2·00	0·312	2·19
652·7	9·4	1·82	39·1	2·11	0·452	3·03
662·7	9·2	1·79	29·6	3·36	1·24	4·98
664·0	6·3	0·96	55·8	2·45	0·412	4·69
669·5	6·7	0·96	22·4	1·52	0·537	7·35
669·5	6·7	1·00	53·5	3·45	0·101	6·46
670·0	9·2	1·74	42·4	5·13	1·79	7·39
670·7	9·15	1·75	52·9	5·62	1·06	6·42
671·0	6·36	1·00	60·9	3·79	1·09	6·41
675·7	6·96	0·99	50·4	3·94	1·12	8·21
676·6	6·97	0·99	31·4	2·86	1·20	9·55
678·6	6·96	0·99	44·0	4·54	1·14	11·2
682·0	6·98	0·99	25·4	2·83	0·70	11·9
684·2	6·98	0·96	40·0	4·05	1·65	11·0
686·3	6·29	0·96	74·3	7·44	4·31	11·0
693·0	6·57	0·97	44·3	9·51	4·89	25·0
695·5	6·53	0·95	47·8	10·13	5·67	25·0
696·5	6·98	1·00	40·8	6·83	3·52	18·3
710·5	6·57	0·90	41·1	14·02	8·95	46·4

* Packed vessel.

$$\log k_9\ (\text{sec.}^{-1}) = (11{\cdot}8 \pm 0{\cdot}08) - (39{,}994 \pm 200/2{\cdot}3\boldsymbol{R}T).$$

It is difficult to see why the *A*-factor should be slightly lower than that calculated for the decomposition of hydrazine itself ($10^{12\cdot2}$ sec.$^{-1}$) and significantly lower than that for other substituted hydrazines[3] ($\sim10^{13}$ sec.$^{-1}$).

Bond Strengths in Hydrazines.—Assuming that E_9 corresponds to $D(\mathrm{PhNH{-}NH_2})$, and knowing the heats of formation of the anilino-radical[2] (47·7 kcal. mole^{-1}) and phenylhydrazine[7] (48·9 kcal. mole^{-1}), the heat of formation of the amino-radical is 41·2 kcal. mole^{-1}. Kerr, Sekhar, and Trotman-Dickenson[3] found $\Delta H_f^\circ\ (\mathrm{NH_2}) = 39{\cdot}8$ kcal. mole^{-1} from the pyrolysis of hydrazine. The activation energy for the decomposition of hydrazine was determined in the pressure-dependent region, and, since the high-pressure activation energy could not be directly measured, 3 kcal. was added to the experimental value to allow for the effect of pressure. Subsequently Schneider and Rabinovitch,[8] in a comprehensive study of the unimolecular isomerisation of methyl isocyanide, have shown that the difference between the low-pressure and high-pressure activation energies for a reaction involving a molecule of this complexity is nearer 2 kcal. Consequently, it now seems that the high-pressure E for the decomposition of hydrazine should be taken as 56·1 and not 57·1 kcal. mole^{-1} as previously suggested.[3] Hence, the heat of formation of the amino-radical derived from the pyrolysis of hydrazine now becomes 39·3 kcal. mole^{-1}, which still agrees, within the experimental errors, with the result obtained here. The value of 39·3 kcal. mole^{-1} is, however, to be preferred on the grounds that it was obtained by a more direct method.

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[8] Schneider and Rabinovitch, *J. Amer. Chem. Soc.*, 1962, **84**, 4215.