expressed as linear combinations of the overall advancements.

$$\Delta \overline{\mathbf{G}} = (RT/V)\mathbf{g}\Delta\boldsymbol{\xi} \qquad \text{(A-3)}$$

In those cases where the activity coefficients are independent of the concentrations of the reactants, the elements of the **g** matrix are

$$g_{\alpha\beta} = g_{\beta\alpha} = \sum_{i=1}^{N} \frac{\nu_{i\alpha}\nu_{i\beta}}{\overline{C}_i} \qquad \text{(A-4)}$$

where $N$ is the total number of different chemical species. It is interesting to note that the diagonal element $g_{\alpha\alpha}$ is simply the inverse of the $\Gamma$ function of the $\alpha$th elementary step ($\Gamma_\alpha^{-1}$). For small perturbations we may write $\Delta\bar{G}_\alpha = -RT\Delta \ln K_\alpha$. The $\Delta C_\alpha$ can therefore be expressed as linear combinations of the $\Delta$ $\ln K_\alpha$'s by taking the inverse of eq A-3 and substituting the resulting expression for $\Delta\boldsymbol{\xi}$ into eq A-2.

$$\Delta\overline{\mathbf{C}} = -\boldsymbol{\nu}\mathbf{g}^{-1}\boldsymbol{\Delta} \ln \mathbf{K} \qquad \text{(A-5)}$$

Since the matrices $\boldsymbol{\nu}$ and $\mathbf{g}^{-1}$ can be written by inspection, eq A-5 provides a convenient means of expressing overall concentration changes in terms of thermodynamic functions for a completely general reaction mechanism.

In the systems of two coupled equilibria discussed in the present paper, the components $A_1$ and $B_1$ participate only in steps "A" and "B," respectively. The matrix $\boldsymbol{\nu}$ is therefore diagonal with $\nu_{11} = a_1$ and $\nu_{22} = b_1$. The elements of $g$ are: $g_{11} = \Gamma_A^{-1}$, $g_{22} = \Gamma_B^{-1}$, $g_{12} = g_{21} = \Sigma_i(c_{iA}c_{iB}/\bar{C}_i) = f$. It follows from the equation $\boldsymbol{\nu}^{-1}\boldsymbol{\Delta}\overline{\mathbf{C}} = -\mathbf{g}^{-1}\boldsymbol{\Delta} \ln \mathbf{K}$ that

$$\Delta A_1/a_1 = -(\Gamma_A^{-1}\Gamma_B^{-1} - f^2)^{-1}(\Gamma_B^{-1}\Delta \ln K_A - f\Delta \ln K_B) \qquad \text{(A-6)}$$

$$\Delta \bar{B}_1/b_1 = -(\Gamma_A^{-1}\Gamma_B^{-1} - f^2)^{-1}(\Gamma_A^{-1}\Delta \ln K_B - f\Delta \ln K_A) \qquad \text{(A-7)}$$

Equations A-6 and A-7 are equivalent to eq 23 and 24 in the text.

## Appendix II. On the Relationships between the Elements of the Secular Determinant and the Coupling Constants for Two-Step Equilibria

Castellan[20] has shown that the relaxation times for any chemical reaction mechanism are the eigenvalues of the matrix **b**, which is defined by

$$-\mathrm{d}\boldsymbol{\Delta\xi}/\mathrm{d}t = \mathbf{b}\boldsymbol{\Delta\xi} \qquad \text{(A-8)}$$

The matrix **b** may be written as a product of two matrices **r** and **g**, where the latter is defined in Appendix I and **r** is a diagonal matrix whose typical element $r_\alpha$ is the exchange rate of the $\alpha$th elementary step. In the systems of two coupled equilibria considered in the present paper, we have $\delta\xi_A = \delta A_1/a_1$, $\delta\xi_B = \delta B_1/b_1$, and therefore the linearized rate equations corresponding to eq A-8 become eq 55 and 56 of the text. The elements of the secular determinant are $b_{11} = r_A\Gamma_A^{-1}$, $b_{12} = r_Af$, $b_{22} = r_B\Gamma_B^{-1}$, and $b_{21} = r_Bf$. It is evident that the ratios $b_{12}/b_{11}$ and $b_{21}/b_{22}$ are equivalent to the coupling constants $\Gamma_Af$ and $\Gamma_Bf$.

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# Very Low Pressure Pyrolysis. V. Benzylamine, *N*-Methylbenzylamine, and *N*,*N*-Dimethylbenzylamine and the Heat of Formation of the Amino, Methylamino, and Dimethylamino Radicals[1a]

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**Abstract:** VLPP studies of the benzyl–amino bond homolysis in benzylamine, *N*-methylbenzylamine, and *N*,*N*-dimethylbenzylamine yield heats of formation of the amino, methylamino, and dimethylamino radicals, respectively, if RRKM or RRK theory is used to relate the low-pressure rate constants measured to the high-pressure Arrhenius parameters. Values of the high-pressure $A$ factors were obtained by analogy with the relevant alkylbenzenes. Heats of formation for the three radicals are 47.2, 45.2, and 38.2 kcal/mol, respectively. These lead to $DH°(NH_2\text{–}H) = 110$, $DH°(CH_3NH\text{–}H) = 103$, and $DH°((CH_3)_2N\text{–}H) = 95$ kcal/mol, all considerably higher than previously reported.

The thermochemical properties and reactivities of simple carbon-centered free radicals have been measured often and are reasonably well known.[2a] There is considerably less information available as to the properties of nitrogen-centered free radicals, and what there is, is subject to a good deal of uncertainty.[2b]

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[1] (a) This work was supported in part by Air Force Rocket Propulsion Laboratory, Contract No. FO-4611-69-C-0096, and in part by the National Aeronautics and Space Administration, Contract No. NAS7-472. (b) Postdoctoral Research Associate.

[2] (a) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968; (b) S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas-Phase Unimolecular Reactions," NSRDS-NBS 21, National Bureau of Standards Reference Data System, U. S. Department of Commerce, 1970; H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinet.*, 1, 221 (1969).

Table I. Previous Data on Benzylamine Pyrolysis

| Molecule | Log ($A_s$/sec$^{-1}$) | $E$, kcal/mol | Products | Log ($A_r/M^{-1}$ sec$^{-1}$) | Log ($A_r'/M^{-1}$ sec$^{-1}$)[a] | Corrected log ($A_s$/sec$^{-1}$)[b] | Corrected $E$, kcal/mol[b] |
|---|---|---|---|---|---|---|---|
| BA | 13.0 | 59.8 | $NH_3$ | 6.6 | 9.0 | 15.3 | 69.8 |
| MBA | 13.4 | 60.0 | $CH_3NH_2$ | 5.9 | 8.7 | 15.7 | 69.0 |
| DMBA | | | No amine | | | | |

[a] Recombination $A$ factor for hydrocarbon analog. [b] Computed Arrhenius parameters for N-compound pyrolysis using $A$ factor for recombination of hydrocarbon analog.

In an attempt to remove this uncertainty (but recognizing the possibility of adding to it), we have used the very low-pressure pyrolysis (VLPP) of benzylamine (BA), *N*-methylbenzylamine (MBA), and *N*,*N*-dimethylbenzylamine (DMBA) to ascertain the heats of formation of the free radicals ($\dot{N}H_2$), $\dot{N}(CH_3)H$, and $\dot{N}(CH_3)_2$, respectively.

Previous work on the pyrolyses of these compounds has been carried out by Kerr, Sekhar, and Trotman-Dickenson[3] using the toluene carrier flow technique. The results of that study are shown in Table I.

Arrhenius parameters reported in ref 3 are tabulated in columns 2 and 3. Both the products attributed to the ensuing reactions with excess toluene and the absence of products that might have been expected to be present are noted in the fourth column.

The entropies of the amines and the benzyl radical are known and those of the amino radicals are easily estimated.[2b] The entropy for bond scission $\Delta S°_{\langle T\rangle}$ is thus known and the $A$ factor for the radical recombination reaction $A_r$ may be computed from the $A$ factor for bond scission $A_s$ and the expression[2b]

$$\log (A_r/M^{-1}\ \text{sec}^{-1}) = \log (A_s/\text{sec}^{-1}) - [\Delta S°_{\langle T\rangle} - R(1 + \ln R'T)]/2.3R$$

where $R$ = 1.99 cal/(mol deg), $R'$ = 0.802 l. atm/(mol deg), and $\Delta S°_{\langle T\rangle}$ = entropy of bond scission (standard state of 1 atm, $T$ °K). These are shown in the fifth column of Table I.

The sixth column of the table shows the value of the recombination $A$ factor for the analogous carbon-centered radicals $A_r'$. (It is usually assumed that $A$ factors for radical recombination are independent of $T$.) In their recent monograph on unimolecular reactions, Benson and O'Neal[2b] take note of the differences between $A_r$ and $A_r'$ and conclude that the reported values of $A_s$ are incorrect. They further conclude that the absolute rate data are probably reliable and recommend activation energies obtained by fitting the reported rate constant at the mean temperature to an Arrhenius equation with a corrected $A_s$ such that the values for $A_r$ are the same as those for the analogous carbon-centered radical. The "corrected" $A$ factors and activation energies of Benson and O'Neal for bond scission are shown in the last two columns in Table I.[4] (Available evidence[5] for $\dot{N}H_2$ radical combination indicates that there is little difference between this rate and that of $CH_3$ radical combination.)

The approach in this work was based on confidence in the Benson and O'Neal prediction of $A$ factors for the bond scission reactions. It was thought desirable to measure the rate constants for these reactions by a method different from that previously employed to see if the modified earlier rate constants did, in fact, lead to the correct activation energies.

The experimental technique used was VLPP. This technique allows the evaluation of high-pressure activation energies from low-pressure rate constants if all the $A$ factors are known.

## Experimental Section

**Materials.** Benzylamine, *N*-methylbenzylamine, and *N*,*N*-dimethylbenzylamine were obtained from Eastman or Baker. These were degassed under vacuum and the heated liquid was used as a source of vapor as described below. No impurities of any consequence were detected with the quadrupole mass spectrometer used as an analytical device for VLPP studies.

Fluorobenzene obtained from Eastman and perfluoroethane purchased from Air Products were used as internal standards.

**Apparatus and Procedures.** The apparatus and theory of VLPP, developed at SRI, have been described in the literature.[6] Briefly, the pyrolysis of a flowing gas in a reactor is described under conditions of very low pressure (*ca.* 0.5–5 $\mu$), such that the molecular flow region is attained. Since, under these conditions gas–gas collisions are few, the system is uncomplicated by secondary reactions such as have taxed earlier studies. Further, under these conditions the average molecule that emerges from the aperture has undergone $Z$ collisions with the fused silica reaction walls, where $Z = A_v/A_h$, the area of the walls of the vessel divided by the area of the exit aperture. Such a system can be treated as a stirred flow reactor and the rate constants for processes occurring within it are simply related to the steady-state concentrations of reactants and products.[6] The exit molecules are analyzed with a quadrupole mass spectrometer.[7]

Given the simple system

$$AB \underset{k_r}{\overset{k_d}{\rightleftarrows}} A + B$$

with no further reactions of any species occurring prior to escape from the reactor[6]

$$k_d = [f/(1 - f)]k_{eAB} = [(I_{AB}{}^0 - I_{AB})/I_{AB}]k_{eAB}$$

where $I_{AB}$ is the intensity at temperature $T$ of given mass peak attributable to AB; $I_{AB}{}^0$ is the intensity of the same peak at a temperature below which no decomposition occurs; and $f$ is the fraction of AB consumed by reaction (see Appendix). The value of the rate constant for escape through the aperture of radius $r_h$ for molecule AB of molecular weight $M_{AB}$ from the vessel of volume $V$ (cm$^3$) is obtained from the kinetic theory of gases

$$k_{eAB} = 3.65 \times 10^3(T/M_{AB})^{1/2}(\pi r_h{}^2/V)\ \text{sec}^{-1}$$

We have shown[6] and recently demonstrated quantitatively[8] that the VLPP technique is a convenient tool for measuring the rate constants of unimolecular processes ($k_d = k_{uni}$).

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[3] J. A. Kerr, R. C. Sekhar, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3217 (1963).

[4] Some of the values of $A_r'$ quoted in ref 2b are incorrect by a few tenths of a power of ten, but the argument is unchanged.

[5] J. D. Salzman and E. J. Blair, *J. Chem. Phys.*, 41, 3654 (1964); S. Gordon, W. Mulac, and P. Nangia, *J. Phys. Chem.*, 75, 2087 (1971).

[6] S. W. Benson and G. N. Spokes, *J. Amer. Chem. Soc*, **89**, 2525 (1967).

[7] The dimensions of the reactor used here are such that $Z \sim 2 \times 10^3$. The reactor is a 2.5-cm wide by 9.5-cm long cylinder, with an exit aperture of 0.1-cm radius (volume ~ 30 cm$^3$).

[8] (a) K. D. King, D. M. Golden, G. N. Spokes, and S. W. Benson, *Int. J. Chem. Kinet.*, 3, 411 (1971); (b) K. D. King, D. M. Golden, and S. W. Benson, unpublished results; (c) P. Beadle, D. M. Golden, and S. W. Benson, unpublished results.

**Table II.** Molecular Parameters Used for RRKM Calculations. Molecular Parameters for $PhCH_2NH_2$, $PhCH_2NHMe$, and $PhCHN_2(Me)_2$

| | $PhCH_2NH_2$ | | $PhCH_2NHMe$ | | $PhCH_2N(Me)_2$ | |
|---|---|---|---|---|---|---|
| | Molecule | Complex | Molecule | Complex | Molecule | Complex |
| Frequencies, $cm^{-1}$, with degeneracy | 3000 (9) | 3000 (9) | 3000 (11) | 3000 (11) | 3000 (13) | 3000 (13) |
| | 1615 (3) | 1615 (3) | 1615 (3) | 1615 (3) | 1615 (3) | 1615 (3) |
| | 1380 (7) | 1380 (7) | 1375 (10) | 1375 (10) | 1380 (14) | 1380 (14) |
| | 1180 (3) | 1180 (3) | 1180 (3) | 1180 (3) | 1180 (3) | 1180 (3) |
| | 1040 (5) | 1035 (3) | 1040 (5) | 1040 (5) | 1040 (5) | 1040 (5) |
| | 965 (3) | 965 (2) | 965 (4) | 965 (3) | 965 (5) | 965 (4) |
| | 865 (2) | 865 (2) | 865 (2) | 865 (2) | 865 (2) | 865 (2) |
| | 765 (3) | 760 (2) | 760 (4) | 760 (2) | 760 (3) | 760 (2) |
| | 660 (2) | 660 (2) | 660 (2) | 660 (2) | 660 (2) | 660 (2) |
| | 450 (3) | 450 (3) | 450 (3) | 450 (3) | 450 (3) | 450 (3) |
| | 350 (2) | 320 (1) | 350 (2) | 320 (1) | 325 (4) | 320 (1) |
| | 180 (2) | 260 (2) | 250 (1) | 230 (2) | 250 (1) | 240 (2) |
| | 30 (1) | 150 (3) | 174 (2) | 155 (3) | 185 (3) | 185 (3) |
| | | 95 (1) | 35 (2) | 75 (2) | 30 (2) | 90 (4) |
| $PhCH_2$–$NR_2$, Å | | 2.47 | | 2.47 | | 2.47 |
| $I_AI_BI_C$, $(g\ cm^2)^3 \times 10^{120}$ | $7.29 \times 10^7$ | $1.22 \times 10^8$ | $1.87 \times 10^8$ | $3.33 \times 10^8$ | $3.82 \times 10^8$ | $6.82 \times 10^8$ |
| $I_{ir}$, $(g\ cm^2) \times 10^{40}$ | | 2.80[a] | | 66.0[a] | | 145[a] |
| Sigma[b] | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |

[a] Using symmetry ≡ "foldness" of barrier = 3. [b] Sigma = $\sigma/n$ where $\sigma$ = symmetry number for external rotation and $n$ = number of optical isomers.

**Table III.** VLPP Data for $PhCH_2NH_2$

| Old reactor | | | | New reactor | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $T$, °K | $I_p$ | % dec | $k_{uni}$[a] | $T$, °K | $I_p$ | % dec | $k_{uni}$[a] | $k_{RRKM}$[a,b] | $k/k_\infty$ (RRKM) |
| 1040 | 140.3 | 8.9 | 1.16 | 1053 | 139.0 | 9.7 | 1.28 | 0.926 | 0.47 |
| 1047 | 138.3 | 10.1 | 1.35 | 1064 | 123.6 | 19.7 | 2.96 | | |
| 1058 | 132.0 | 14.2 | 1.99 | 1074 | 109.8 | 28.6 | 4.86 | | |
| 1068 | 127.2 | 17.3 | 2.53 | 1092 | 123.6 | 19.7 | 3.00 | 2.69 | 0.40 |
| 1076 | 119.3 | 22.4 | 3.51 | 1100 | 118.7 | 22.9 | 3.64 | | |
| 1085 | 114.7 | 25.4 | 4.15 | 1109 | 111 | 27.9 | 4.76 | 4.14 | 0.37 |
| 1090 | 110.2 | 28.3 | 4.83 | 1121 | 100.8 | 34.5 | 6.52 | | |
| 1097 | 107.6 | 30.0 | 5.26 | 1129 | 96 | 37.6 | 7.49 | | |
| 1104 | 103.6 | 32.6 | 5.95 | 1144 | 86.11 | 44.0 | 9.84 | 9.53 | 0.31 |
| 1114 | 99.36 | 35.4 | 6.77 | 1166 | 76.58 | 50.2 | 12.7 | | |
| 1123 | 94.90 | 38.3 | 7.70 | 1176 | 60 | 61.0 | 19.8 | 19.2 | 0.27 |
| 1132 | 86.02 | 44.1 | 9.81 | 1191 | 54.35 | 64.7 | 23.3 | | |
| 1141 | 81 | 47.4 | 11.2 | 1200 | 44 | 71.4 | 31.9 | 31.4 | 0.24 |
| 1150 | 75.85 | 50.7 | 12.9 | 1213 | 43.76 | 71.5 | 32.3 | | |
| 1161 | 73 | 52.5 | 13.9 | 1218 | 41.25 | 73.2 | 35.2 | | |
| 1173 | 65.72 | 57.3 | 16.9 | 1223 | 33 | 78.5 | 47.3 | 48.8 | 0.21 |
| 1179 | 63.90 | 58.5 | 17.8 | 1229 | 33.17 | 78.4 | 47.1 | | |
| 1184 | 53 | 65.5 | 24.2 | 1236 | 26.82 | 82.5 | 61.5 | | |
| 1195 | 50.56 | 67.1 | 26.1 | 1248 | 20.52 | 86.6 | 84.8 | 76.8 | 0.19 |
| 1207 | 45.68 | 70.3 | 30.4 | 1251 | 21 | 86.3 | 82.7 | | |
| 1220 | 40.80 | 73.5 | 35.7 | 1255 | 20.52 | 86.6 | 85.0 | | |
| 1230 | 37.10 | 75.9 | 40.8 | 1258 | 18.54 | 87.9 | 95.6 | | |
| 1241 | 33.53 | 78.2 | 46.7 | | | | | | |
| 1250 | 28.32 | 81.6 | 57.9 | | | | | | |

[a] $Sec^{-1}$. [b] See Table II for molecular parameters.

As unimolecular rate constants are pressure dependent, the VLPP measured rate constant $k_{uni}$ is in general not equal to the high-pressure limiting rate constant $k_\infty$. Thus the temperature dependence of the measured rate constant does not yield $A_\infty$ and $E_\infty$, the universal parameters of the reaction that are defined by

$$k_\infty = A_\infty 10^{-E_\infty/\theta}$$

where $\theta = 2.303RT$ in kcal/mol.

A means is required for converting $k_{uni}$ to $k_\infty$, so that $k_{uni}$ may be predicted under any conditions of pressure and temperature. Such means have existed for quite some time in the form of the Rice–Ramsperger–Kassel (RRK) theory and the modification of this theory by Marcus (RRKM).[9]

The experimental values of $k_{uni}$ are compared with predicted values based on assigned kinetic parameters using both RRK and RRKM theories and assuming unit collisional efficiency for the wall–gas collisions.

High-pressure Arrhenius $A$ factors ($A_\infty$) were computed from the corresponding partition functions for the active molecule and transition complex. The predicted $A_\infty$ values were chosen for the benzylamines by assigning frequencies to the molecules and transition states in direct analogy to those for alkylbenzenes[10] (see Table II). These latter were themselves determined by forcing the known rate constant data[2b] to fit an Arrhenius equation whose activation energy corresponded properly to the known[2a] bond dissociation energies of the alkyl-benzyl bonds.

The model transition states thus chosen were found to correspond in all cases to a lengthening of the breaking bond by 1.0 Å, a lower-

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(9) K. J. Laider, "Chemical Kinetics," McGraw-Hill, New York, N. Y., 1965.

(10) The assignments for alkylbenzenes and the analogous benzylamines differ by one C–H stretch and two H-atom bending motions which are essentially the same in all the compounds and all the transition states.

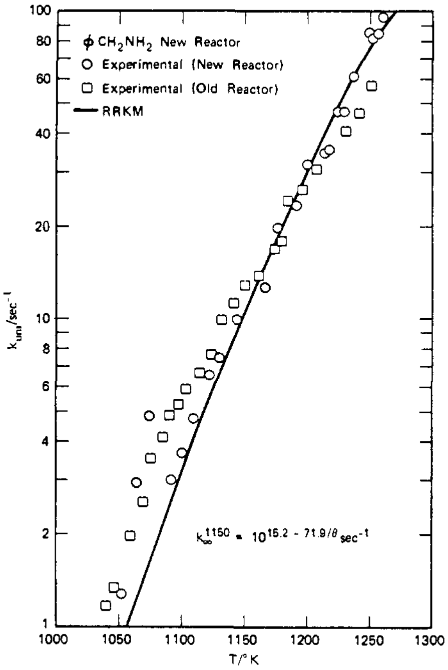

Figure 1. Rate constants for the reaction $PhCH_2NH_2 \rightarrow Ph\dot{C}H_2 + \dot{N}H_2$.

ing of the alkyl-benzyl rotation barrier to zero, a stiffening of the $\varphi$-$CH_2$ internal rotation, and the reduction in frequency of the four molecular rocking modes that become external rotations of the product radicals. This reduction was shown to be to 25% for benzylamine (ethylbenzene) and 30% of the original frequency for the others.

Using an RRKM computer program kindly supplied by Professor B. S. Rabinovitch of the University of Washington, $k_{uni}$ has been calculated as a function of temperature at a collision frequency corresponding to the frequency of gas-wall collisions in the VLPP reactor ($\omega = Zke = 7.7 \times 10^3(T/M)^{1/2}$), the value of the "critical energy" being chosen by the best fit to the data. The critical energy and the frequencies enable the calculation of the Arrhenius activation energy at mean reaction temperature ($E(T)$).

The RRK values were obtained by interpolation of Emanuel's tables[11] using the $A_\infty$ values at the mean temperatures, values of the parameter $s$ defined[12] as $s \equiv C_{vib}(T)/R$, and chosing the activation energy from a fit to the data. These values are not reported here, but they give results insignificantly different from the RRKM values.

## Results

Qualitative descriptions of the VLPP of each of the amines is outlined below, followed by Tables III–V which show quantitative rate constant data based on disappearance of molecular peaks.

Figures 1–3 show $k_{uni}$ as a function of temperature and compare experimental results with RRKM theory.

$k_{uni}$ is independent of flow rate in the range *ca.* 5 × $10^{15}$ to 5 × $10^{16}$ molecules/sec employed here.

**Benzylamine (BA).** The mass spectrum of pyrolyzing BA shows a decrease in molecular (107) and molecular − 1 (106), as well as the appearance of and increase in peaks for toluene (91 and 92) and $NH_3$ (17). These observations suggest that C–N scission is taking place.

$$PhCH_2NH_2 \longrightarrow Ph\dot{C}H_2 + \cdot NH_2$$

Since free radicals which effuse from the reactor make many collisions with the walls of the pumping chamber before reaching the ionizer of the mass spectrometer, we expect free radicals R to appear as RH. Thus the appearance of toluene and $NH_3$ is consistent with expectations for homolytic C–N bond scission.

Table IV. VLPP Data for $PhCH_2NHMe$

| $T$, °K | $I_p$ | % dec | $k_{uni}$[a] | $k_{RRKM}$[a,b] | $k/k_\infty$ (RRKM) |
|---|---|---|---|---|---|
| 1008 | 135 | 10.5 | 1.30 | 0.963 | 0.63 |
| 1025 | 128 | 15.2 | 1.99 | | |
| 1041 | 117 | 22.5 | 3.25 | 2.46 | 0.56 |
| 1054 | 108 | 28.4 | 4.48 | | |
| 1067 | 97 | 35.7 | 6.31 | 5.21 | 0.51 |
| 1079 | 88 | 41.7 | 8.16 | | |
| 1085 | 80 | 47.0 | 10.1 | 8.29 | 0.47 |
| 1093 | 71 | 52.9 | 12.9 | | |
| 1101 | 69 | 54.3 | 13.6 | 12.3 | 0.44 |
| 1107 | 60 | 60.2 | 17.5 | | |
| 1119 | 47 | 68.8 | 25.7 | 18.8 | 0.41 |
| 1131 | 44 | 70.8 | 28.4 | | |
| 1136 | 40 | 73.5 | 32.4 | 27.6 | 0.38 |
| 1152 | 36 | 76.1 | 37.6 | | |
| 1157 | 32 | 78.8 | 43.9 | 43.4 | 0.34 |
| 1164 | 30 | 80.1 | 47.7 | | |
| 1175 | 26 | 82.7 | 57.2 | 62.6 | 0.31 |
| 1183 | 24 | 84.1 | 63.2 | | |
| 1187 | 22 | 85.4 | 70.1 | | |

[a] $Sec^{-1}$. [b] See Table II for molecular parameters.

Table V. VLPP Data for $PhCH_2N(Me)_2$

| $T$, °K | $I_p$ | % dec | $k_{uni}$[a] | $k_{RRKM}$[a,b] | $k/k_\infty$ (RRKM) |
|---|---|---|---|---|---|
| 833 | 133.8 | 8.32 | 0.887 | 0.908 | 0.70 |
| 913 | 125 | 13.9 | 1.61 | | |
| 919 | 109 | 25.1 | 3.35 | 3.13 | 0.61 |
| 929 | 101 | 30.4 | 4.39 | | |
| 935 | 83.3 | 42.9 | 7.56 | | |
| 944 | 72.1 | 50.5 | 10.32 | 6.86 | 0.56 |
| 956 | 58.0 | 60.2 | 15.39 | | |
| 966 | 50.7 | 65.2 | 19.16 | 1.1 | 0.50 |
| 978 | 46.2 | 68.3 | 22.20 | | |
| 988 | 39.7 | 72.7 | 27.59 | 23.9 | 0.45 |
| 995 | 33.0 | 77.3 | 35.42 | | |
| 1005 | 26.9 | 81.5 | 46.00 | 37.0 | 0.42 |
| 1013 | 25.9 | 82.2 | 48.34 | | |
| 1025 | 20.5 | 85.8 | 64.11 | 60.3 | 0.37 |
| 1033 | 18.9 | 87.0 | 70.71 | | |
| 1041 | 15.8 | 89.1 | 87.10 | | |
| 1052 | 13.2 | 90.2 | 106.66 | 111.4 | 0.32 |
| 1058 | 11.7 | 91.9 | 121.89 | | |

[a] $Sec^{-1}$. [b] See Table II for molecular parameters.

Further support of this suggestion comes from the observation that the simultaneous addition of $NO_2$ to the pyrolysis chamber results in the appearance of large peaks for benzaldehyde (106) and $H_2O$, attributed to the very rapid reactions

$$Ph\dot{C}H_2 + NO_2 \longrightarrow PhCH_2O\cdot + NO$$

$$PhCH_2O\cdot \longrightarrow PhCHO + H$$

$$\cdot H + NO_2 \longrightarrow \cdot OH + NO$$

$$\cdot OH + RH \longrightarrow H_2O + R\cdot$$

Also, the addition of $CH_3$ radicals *via* the pyrolysis of di-*tert*-butyl peroxide leads to ethylbenzene formation.

The $C_2F_6$ peak at 119 amu was used as an internal standard. Variation of ionizing voltage from ~9 to 70 eV did not affect the value of the rate constant.

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[11] Tables of the Kassel Integral, prepared by G. Emanuel, A. F. Report No. SAMSO-TR-6936, 1969 (Aerospace Corp.).

[12] D. M. Golden, R. K. Solly, and S. W. Benson, *J. Phys. Chem.*, 75, 1333 (1971).

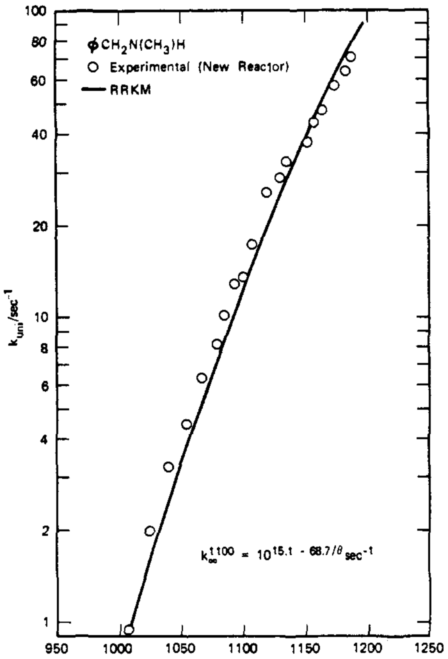

Figure 2. Rate constants for the reaction $\mathrm{PhCH_2NHCH_3} \rightarrow \mathrm{Ph\dot{C}H_2} + \mathrm{\dot{N}HCH_3}$.

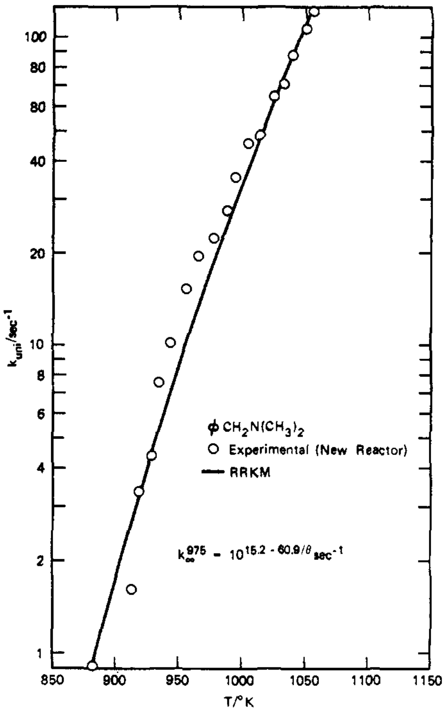

Figure 3. Rate constants for the reaction $\mathrm{PhCH_2N(CH_3)_2} \rightarrow \mathrm{Ph\dot{C}H_2} + \mathrm{\dot{N}(CH_3)_2}$.

During the study of BA, the reactor inlet capillaries were enclosed in a silica envelope. This modification enabled these inlet capillaries to be water- or air-cooled and thus removed the possibility of chemical reaction prior to the main reactor. Rate constants obtained in the modified vessel were the same as those obtained previously.

***N*-Methylbenzylamine (MBA).** Over the temperature range 700–1000°, rate constants were determined from the decrease in molecular (121 amu) intensity. The product spectrum showed the formation of both $\mathrm{CH_3NH{-}H}$ and $\mathrm{PhCH_2{-}H}$ as expected, except that at temperatures corresponding to $\geq 40\%$ decomposition, the 31-amu peak ($\mathrm{CH_3NH_2}$) begins to diminish as the radicals $\mathrm{CH_3\dot{N}H}$ evidently decompose to $\mathrm{CH_2{=}NH} + \mathrm{H}$.

***N*,*N*-Dimethylbenzylamine (DMBA).** In preliminary runs, rate constants were measured from the decrease in 135, 134, and 58 amu (molecular, molecular − 1, and molecular less phenyl fragment) peak intensities at temperatures between 404 and 873°. Fluorobenzene (96 amu) was used as an internal standard.

Products were toluene (92 amu), $\mathrm{H_2}$ (2 amu), and a product having peaks at 43 and 42 amu ascribed to $\mathrm{CH_3{-}N{=}CH_2}$ (43 amu). The last arises from the reaction

$$\mathrm{(CH_3)_2N\cdot} \longrightarrow \mathrm{\cdot H} + \mathrm{CH_2{=}NCH_3}$$

In later experiments the disappearance of the molecular peak (135 amu) was measured as a function of temperature. The 138-amu molecular peak of $\mathrm{C_2F_6}$ was used as an internal standard. The results were in good agreement with those obtained earlier from the 58- and 135-amu peaks.

The addition of $\mathrm{NO_2}$ shows an increase in benzaldehyde and $\mathrm{H_2O}$ which, as explained above for benzylamine, points to bond scission and radical formation as the mechanism of the reaction.

The source of the observed $\mathrm{H_2}$ is likely due to abstraction of hydrogen by H· from RH. However, the fact that the addition of $\mathrm{NO_2}$ had only a small effect on the $\mathrm{H_2}$ peak makes the issue somewhat obscure.

## Discussion

The experimental evidence clearly indicates that the benzylamine pyrolyses are bond scission reactions. The heats of formation at 298°K of the amino radicals, $\mathrm{NH_2}$, $\mathrm{CH_3NH}$, and $\mathrm{(CH_3)_2N}$, were obtained from the $E_\infty$ (298°K) values for the pyrolyses of BA, MBA, and DMBA, respectively, given the experimentally based assumption that the activation energy of each of the reverse (combination) reactions is zero at 298°K,[13] when the rate constant is measured in molar concentration units. Then $E_\infty$ (298°K) = $\Delta H°_{298} - 0.6$ for the bond breaking reaction, and since the heats of formation of the benzylamines and the benzyl radical are known,[2a] the values for the amino radicals can thus be computed. These parameters are shown in Table VI.

The values of the heat of formation of amino radicals found in this work lead to a prediction that the high-pressure Arrhenius rate constant for hydrazine N–N bond rupture would be

$$\log (k_{1000}/\mathrm{sec^{-1}}) \cong 17.8 - 74/\theta$$

These Arrhenius parameters are considerably different from the currently accepted values and are thus of extreme importance. Setser and Richardson[14] had recognized that the reported *A* factors were incorrect and proposed a very different value based on their avail-

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(13) This procedure ignores the problem created by making the activation energies of radical combination reactions zero at 298°K, namely, that this procedure implies a negative value for the same quantity at lower temperatures. A discrepancy is thus created of the order of 1–2 kcal/mol, which may be a measure of the uncertainties involved.

(14) D. W. Setser and W. C. Richardson, *Can. J. Chem.*, **47**, 2593 (1969).

**Table VI.** Arrhenius Parameters for BA, MBA, and DMBA C–N Homolysis and the Heats of Formation of the Amino Radicals Calculated Therefrom

| Molecule | Log $A(T)$,[a] sec$^{-1}$ | $E(T)$,[a] kcal/mol | Log $A$ (298°), sec$^{-1}$ | $E$(298°), kcal/mol | $\Delta H°_{298}$, kcal/mol | $\Delta H_f°_{298}$ ($R_2N\cdot$), kcal/mol |
|---|---|---|---|---|---|---|
| BA | 15.2 | 71.9 | 14.6 | 70.6 | 71.2 | 47.2 |
| MBA | 15.1 | 68.7 | 14.8 | 68.1 | 68.7 | 45.2 |
| DMBA | 15.2 | 60.9 | 15.0 | 60.6 | 61.2 | 38.2 |

[a] Parameters for the mean reaction temperature, $T$.

able data for second-order $NH_2$ radical recombination from flash photolysis experiments.[5] Unfortunately, they failed to recognize that the heat of formation of $NH_2$ radicals upon which they based their activation energy estimate came from the same sources as provide incorrect $A$ factors! We shall discuss this further in a subsequent manuscript.[15]

The values of the heats of formation of the amino radicals measured in this work lead to values of the bond dissociation energies $DH°(NH_2\text{–}H)$, $DH°(CH_3NH\text{–}H)$, and $DH°(CH_3)_2N\text{–}H$, which, when considered from the viewpoint of the periodic table as shown in Table VII, are inherently more satisfying than the older values[3] shown in parentheses.

**Table VII**

| | | | |
|---|---|---|---|
| $CH_3$–H<br>104 | $NH_2$–H<br>110<br>(103) | HO–H<br>119 | F–H<br>134 |
| $CH_3CH_2$–H<br>98 | $CH_3NH$–H<br>103<br>(92) | $CH_3O$–H<br>104 | |
| $(CH_3)_2CH$–H<br>95 | $(CH_3)_2N$–H<br>96<br>(86) | | |
| $(CH_3)_3C$–H<br>92 | | | |

A recent[16] value of the activation energy for the reaction

$$O + NH_3 \longrightarrow \dot{N}H_2 + \dot{O}H$$

of 6.6 kcal/mol, when combined with the usual assumption that the reverse, exothermic, radical disproportionation process would have no activation energy, yields a value for $\Delta H_f°(NH_2)$ of 46 kcal/mol in excellent agreement with our own value of 47.2 kcal/mol.

Several other values[17] exist for the values of heats of formation of amino radicals. Most are from appearance potential measurements and error limits tend to be at least ±5 kcal/mol. Furthermore, the actual values of the appearance potentials are usually obtained from extrapolation of curves which makes the value even more questionable. In some of these papers, the values depend on taking the toluene carrier value for the decomposition of hydrazine as being correct.

The values of the thermochemical quantities for the amino radicals measured in this work allow the computation of equilibrium constants for the dissociation of the benzylamines studied. Given the considerations of the Appendix, one might have expected the amine decompositions to be flow dependent. They were not. This is easily explained in the cases of MBA and DMBA as due to the decomposition of the methylamino and radicals, respectively. In the case of BA itself, this lower value is probably evidence for the rapid disproportionation of $NH_2$ radicals which has been seen in other studies.[5]

**Error Limits.** We estimate conservatively that the heats of formation of the radicals reported herein should be *ca.* ±2 kcal/mol. This estimate is arrived at by noting that with the fixed $A$ factors used here the scatter of the measured rate constants allows for errors of *ca.* ±0.5 kcal/mol, errors in the fixed $A$ factors can account for another *ca.* ±0.5 kcal/mol, and uncertainties introduced in the geometrical calculations used to determine $\omega$ and $k_e$ could introduce the same sort of error. Taking these all into account, and adding some to reflect other random and systematic uncertainties, leads to the ±2 kcal/mol estimate.

## Appendix

In the case that A and B are free radicals, one must consider the entire system including all the possible combination and disproportionation reactions which lead to the relationship

$$k_d = [f/(1 - f)]k_{eab}/(1 - \gamma)$$

$$\gamma = \frac{\mu_{AB}^{1/2}}{k_{eab}}K_{rd}\left[k_{eab}(AB)\left(\frac{f}{1-f}\right)^2 - (\alpha + \beta)\frac{f}{1-f} + \frac{\alpha\beta}{k_{eab}(AB)}\right]$$

$$\mu_{AB} = (M_A M_B)/M_{AB}^2 \text{ for A = B (chemically)} = 2 \text{ for A} \equiv \text{B (chemically)}$$

$$K_{rd} = k_r/k_d$$

$$\alpha = 2k_{ea2}(A_2) + k_{ea+h}(A)_{+H} + k_{ea-h}(A_{-H})$$

$$\beta = 2k_{eb2}(B_2) + k_{eb+h}(B_{+H}) + k_{eb-h}(B_{-H})$$

While $\gamma$ looks like a formidable correction to make, it is quite simply related to experiments since for any species M, the observed peak intensity $I_M$ is given by

$$I_M = \alpha_M k_{em}(M)$$

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(15) R. K. Solly, D. M. Golden, and S. W. Benson, unpublished results; presented in part at the 160th National Meeting of American Chemical Society, Chicago, Ill., Sept 1970, Abstract, PHYS 099.

(16) M. J. Kurylo, *et al.*, *J. Chem. Phys.*, 51, 4497 (1969).

(17) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Diaxl, and F. H. Field, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS-26, National Bureau of Standards Reference Data System, U. S. Department of Commerce, 1969.

$\alpha_M$ being the spectrometer sensitivity to M and (M) is the steady state concentration of M in the reactor. Thus, one obtains $\gamma$ by measuring the steady-state amounts of AB, $A_2$, $B_2$, $A_{-H}$, $A_{+H}$, $B_{-H}$, and $B_{+H}$, and by knowing or estimating the equilibrium constant $K_{rd}$.

It is important to note that if the correct value of is used, $k_d$ will be independent of flow rate at a given temperature. Therefore, one knows when one has the correct value of $\gamma$. One may then use various estimates of

$$K_{rd} = 10^{\Delta S_{rd}/4.58\Delta H_{rd}/\theta}$$

to achieve the correct $\gamma$.

This procedure alone may enable a choice to be made as to correct thermochemical parameters when differences which would lead to values of $K_{rd}$, differing by a factor of 10 or so, are in question.

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# Group IVb Metalloidal and Mercury Substituent Effects in the Naphthalene System by Fluorine-19 Nuclear Magnetic Resonance[1]

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*Contribution from the School of Physical Sciences,*
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*Brisbane, Queensland, Australia.* *Received March 4, 1971*

**Abstract:** A number of substituted $\alpha$ (1)- and $\beta$ (2)-fluoronaphthalenes with metallo substituents of the type $MR_3$ (when M is a group IVb metalloid; R = methyl) and HgX (X = halogen or aryl) in the 4, 6, and 7 positions have been synthesized and their fluorine nmr spectra have been measured. The $^{19}F$ substituent chemical shift data (the extent to which a substituent electronically perturbs the C–F neighborhood is indicated by the substituent chemical shift (SCS), which is defined as the difference between the chemical shift of the unsubstituted fluoroaromatic and the substituted fluoroaromatic) provide experimental evidence for $d_\pi$–$p_\pi$ and $6p_\pi$–$p_\pi$ conjugative electron withdrawal (−M) in the ground state by the metalloidal and mercuri substituents, respectively. Comparisons with SCS data from metallo-substituted fluorobenzenes and fluorobiphenyls suggest that this conjugating ability depends on the energy and size of the outer lying orbital with $\pi$ symmetry. This supports previous conclusions concerning the electronic behavior of metalloidal substituents as well as providing additional insight into the nature of aryl–carbon–mercury bonds. Further, the data from the 7$\beta$ disposition suggest that certain approaches to the analysis of $^{19}F$ SCS may be invalid. SCS information from two dicyclopentadienyltitanium derivatives indicates that hyperconjugation is probably an unnecessary concept to invoke for ground-state alkyl substituent effects.

The widespread applicability of fluorine-19 substituent chemical shifts (SCS) for investigating ground-state substituent–substrate interactions[3,4] now extends to many organometallic derivatives from which information on the electronic behavior of metallo-type substituents provides valuable insight into the nature of aryl–carbon–metal bonds.[5] As part of a general program on metallo substituent effects, we have recently utilized the technique to investigate the ground-state electronic properties of mercuri substituents (HgX and $CH_2HgX$ where X = aryl or halogen)[5b,c] as well as metalloidal substituents of the $MR_3$ and $CH_2MR_3$ type where M is a group IVb metalloid (R = methyl or phenyl).[5e] From these studies we concluded that in mono- and bisphenylmercury systems there is little net movement of $\pi$ charge either in or out of the phenyl ring (*i.e.*, there is no detectable ground-state resonance interaction), whereas with substituents of the $MR_3$ type the firm conclusion made was that all the groups engage in conjugative electron withdrawal (−M) *via* $d_\pi$–$p_\pi$ interaction with an adjacent aryl system, the degree of conjugative interaction being not only a sensitive function of d-orbital size but also a function of the adjacent aromatic system. However, the conclusion for the mercury systems was based essentially on the small difference between the meta and para SCS without due consideration to the "anomalous" behavior of substituents in unconjugated positions. On the basis of a simple inductive model and the fact that mercuri substituents (HgX) are more electropositive[5b,c] than the methyl substituent, it could be concluded that considerable mesomeric electron withdrawal occurs *via* vacant

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(1) A preliminary account has been published: W. Adcock and W. Kitching, *Chem. Commun.*, 1163 (1970).

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(4) (a) M. J. S. Dewar and A. P. Marchand, *ibid.*, **88**, 3318 (1966); (b) W. Adcock and M. J. S. Dewar, *ibid.*, **89**, 379 (1967); (c) M. J. S. Dewar and T. J. Squires, *ibid.*, **90**, 200 (1968); (d) G. L. Anderson and L. M. Stock, *ibid.*, **91**, 6804 (1969); (e) W. Adcock, P. D. Bettess, and S. Q. A. Rizvi, *Aust. J. Chem.*, **23**, 1921 (1970).

(5) (a) G. W. Parshall, *J. Amer. Chem. Soc.*, **88**, 704 (1966); (b) W. Adcock, B. F. Hegarty, W. Kitching, and A. J. Smith, *J. Organometal. Chem.*, **12**, 21 (1968); (c) W. Kitching, W. Adcock, and B. F. Hegarty, *Aust. J. Chem.*, **21**, 2411 (1968); (d) R. P. Stewart and P. M. Treichel, *J. Amer. Chem. Soc.*, **92**, 2710 (1970), and references cited therein; (e) A. J. Smith, W. Adcock, and W. Kitching, *ibid.*, **92**, 6140 (1970); (f) R. G. Adler and M. F. Hawthorne, *ibid.*, **92**, 6174 (1970).