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# Modeling Nitrogen Evolution during Coal Pyrolysis Based on a Global Free-Radical Mechanism

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A global free-radical mechanism and an associated rate equation for the evolution of light gas nitrogen during coal devolatilization are presented. The light gas nitrogen rate equation was used to modify an existing nitrogen model so that only a network devolatilization model and coal-specific chemical structural input data are required to adequately predict light gas nitrogen release at a variety of pyrolysis conditions. Model predictions show good agreement with nitrogen release data from pyrolysis of coals of rank from lignite to low volatile bituminous at heating rates from 0.5 to  $10^5$  K/s, temperatures as high as 2300 K, and residence times from 18 ms to 30 min. Good agreement is also achieved with measurements of the nitrogen per aromatic site in partially devolatilized chars. The modified nitrogen model is the first to describe the rank dependence of nitrogen release as light gas without the use of correlations. The model is also the first to offer reasonable explanations for the observed release of ring nitrogen at relatively low temperatures and the inherent stability of much of the char nitrogen during pyrolysis.

## Introduction

As the pulverized-coal combustion industry faces increasingly stringent  $\text{NO}_x$  emission regulations, cost-effective low- $\text{NO}_x$  strategies such as local fuel/air staging may be more important than ever before.<sup>1</sup> Because most coal combustion  $\text{NO}_x$  originates in the coal, proper prediction of the rate of nitrogen evolution from coal during devolatilization is critical to efforts to model these low- $\text{NO}_x$  technologies.

It is believed that, in most coals, nearly all of the nitrogen is contained within the aromatic rings.<sup>2–4</sup> During pyrolysis, nitrogen is thought to be released from coal char in two ways: (1) nitrogen is transported away within the tar aromatic clusters as they vaporize; and (2) nitrogen is released from the char as light gas because of ring rupture.<sup>5</sup> Models that quantitatively predict the rate of pyrolytic nitrogen release as light gas have been formulated for use with the FG-DVC, FLASH-CHAIN, and Chemical Percolation Devolatilization (CPD) network models.<sup>6–9</sup> Each of these nitrogen release

models describes light gas nitrogen release as a first-order process with a distribution of activation energies.

Many researchers have observed that low-rank coals produce more light gas nitrogen than do high-rank coals at the same condition.<sup>6,10–12</sup> Current nitrogen release models empirically correlate the light gas nitrogen release rate equation parameters with parent coal elemental composition in order to describe this rank dependence. Because the chemistry of nitrogen release is not well understood, no attempt is made by these models to describe the chemistry responsible for the variations in light gas nitrogen release with coal type.

The temperature dependence of pyrolytic light gas nitrogen release is unusual in two ways. First, pyrolytic light gas nitrogen release from coal begins at temperatures (about 900–1000 K)<sup>13,14</sup> that are much lower

\* Corresponding author.

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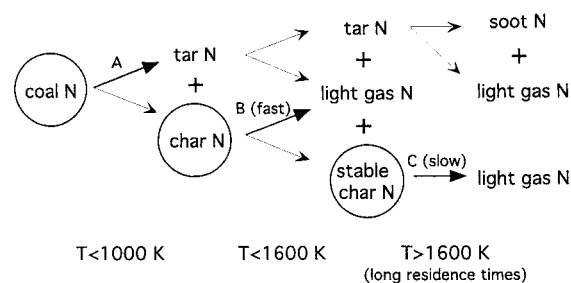
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than those for which thermal decomposition of nitrogen-containing aromatic rings is expected to begin. For example, thermal decomposition is not significant in pure pyrrole until about 1200 K<sup>15</sup> and in pure pyridine until about 1300 K.<sup>16</sup> Second, the rate of pyrolytic light gas nitrogen release slows dramatically once mass release is complete, leaving a large portion of the coal nitrogen in the fully devolatilized char unless treated at very high temperatures (i.e., 2000 K) for long residence times (on the order of minutes).<sup>17,18</sup> These two features of the temperature dependence of pyrolytic light gas nitrogen release have been imitated in previous models<sup>6,19</sup> by using a wide distribution of activation energies with a relatively low mean value. For example, the average activation energy used in FLASHCHAIN for light gas nitrogen release is about 50 kcal/mol,<sup>7</sup> similar to the values measured by Bassilakis and co-workers,<sup>6</sup> with a standard deviation of 16 kcal/mol. In contrast, the C–N bond energy in pyrrole is estimated to be 90 kcal/mol, and the activation energy for pyrrole thermal decomposition is about 70 kcal/mol.<sup>15</sup> Reaction rates of other nitrogen structures may have even higher activation energies. Current nitrogen release models offer no explanation as to why the temperature dependence of nitrogen release via ring rupture during coal devolatilization deviates so markedly from what is expected on the basis of model compound studies.

A nitrogen model is proposed here that includes a new low-activation-energy, low-temperature mechanism in which light gas nitrogen release is initiated by the thermal decomposition of aliphatic side chain material. In addition, a high-activation-energy pure thermal decomposition mechanism is included to explain the high-temperature release of all char nitrogen<sup>17</sup> at very long residence times (i.e., minutes). At shorter residence times, the char nitrogen appears to become "stable" once mass release ceases, since the lower-activation-energy nitrogen release process also ceases.

### Model Development

Nitrogen release with the tar is generally thought to be proportional to the amount of tar release. The tar release mechanism seems to be relatively well understood. Nitrogen release as light gas (such as HCN and NH<sub>3</sub>) from the remaining char is not well understood. As mentioned above, simple ring rupture and release of light gas nitrogen species seems to occur at temperatures lower than expected on the basis of model compound studies. Perry<sup>20</sup> compared results from several model compound studies,<sup>15,16,21</sup> finding that model



**Figure 1.** Schematic showing the fate of coal nitrogen at various stages of pyrolysis. The three pathways included in the nitrogen model of this study are indicated by bold arrows. The temperature ranges where these pathways are important are also indicated.

compounds containing aliphatic attachments released nitrogen more easily than model compounds that contained no aliphatic material. This is evidence that the presence of aliphatic attachments may change the mechanism by which nitrogen is released via ring rupture. Perry<sup>20</sup> discussed how a mechanism of alkyl radical attack on nitrogen heteroatoms is consistent with known reaction mechanisms and how such a free-radical mechanism would lower the activation energy of nitrogen evolution reactions. However, free-radical attack is not important at high temperatures and long residence times; hence, a high-temperature reaction is needed. Three mechanisms of nitrogen release during devolatilization are therefore postulated:

(A) Tar: Nitrogen-containing tar clusters transport nitrogen away from the char during tar release.

(B) Fast light gas: Reaction of ring nitrogen occurs quickly and at temperatures as low as 1000 K through attack of free radicals in the char.

(C) Slow light gas: Ring nitrogen is slowly released from the char clusters at very high temperatures by thermal decomposition leading to rupture of nitrogen-containing rings.

These three pathways are illustrated in Figure 1. In this model, tar clusters are assumed to have the same average structural properties as the char clusters from which they were released, including the average molecular weight per cluster, average aromatic mass per cluster, and the mass of nitrogen per aromatic mass. If the fraction of mass that is aromatic in the parent coal is known, any devolatilization model that can correctly predict changes in the char molecular weight per cluster throughout devolatilization can be used with this nitrogen model. In this study, the Chemical Percolation Devolatilization (CPD) model<sup>8,9</sup> was used to track changes in average char and tar structural properties throughout devolatilization.

Rate equations representing the two parallel mechanisms for light gas nitrogen release were implemented into the previously published nitrogen model of Genetti and Fletcher,<sup>8</sup> replacing their rate equation for HCN formation. The resulting nitrogen model was then used for the predictions shown in this study. The nitrogen model of Genetti and Fletcher<sup>8</sup> was developed and evaluated using <sup>13</sup>C NMR chemical structural data on coals and chars. In this paper, a similar approach was taken, using additional <sup>13</sup>C NMR chemical structural data.

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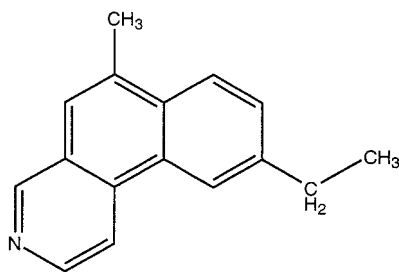
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(19) Niksa, S. *Twenty-Fifth Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1994; pp 537–544.

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(21) Hamalainen, J. P.; Aho, M. J.; Tummavuori, J. L. *Fuel* **1994**, *73*, 1894–1898.



**Figure 2.** Hypothetical cluster in a coal char or tar with 13 aromatic carbons, 3 aliphatic carbons, 1 nitrogen heteroatom, 7 aromatic hydrogens, and 8 aliphatic hydrogens.

The model must account for the amount of nitrogen in the aromatic portion of the remaining char, as this determines (a) the amount of nitrogen released at any moment with the tar and (b) the amount of nitrogen remaining in the char that would be susceptible to release as light gas. As described by Genetti and Fletcher,<sup>8</sup> a useful parameter for describing the aromatic ring nitrogen concentration throughout devolatilization is the nitrogen mass per aromatic mass ( $N_{\text{site}}$ ), defined as

$$N_{\text{site}} = Y_{\text{N}} \left( \frac{M_{\text{cl}}}{M_{\text{site}}} \right) \quad (1)$$

where  $Y_{\text{N}}$  is the mass fraction of nitrogen in the char on a dry ash free basis,  $M_{\text{site}}$  is the measured average aromatic mass per cluster, and  $M_{\text{cl}}$  is the measured average total mass per cluster. These variables can be easily determined from the simple cluster shown in Figure 2. The term cluster means a group of aromatic carbon atoms plus any aliphatic attachments, whereas a site refers to only the aromatic portion of a cluster. Therefore, the mass of the aromatic site of the cluster in Figure 2 (i.e.,  $M_{\text{site}}$ ) consists of the three aromatic rings and the associated hydrogens;  $M_{\text{site}}$  is therefore  $13 \times 12 + 1 \times 14 + 7 \times 1 = 177$  amu. In contrast, the mass per cluster ( $M_{\text{cl}}$ ) would contain both the aliphatic and aromatic material, which, for the cluster shown in Figure 2, would be 221 amu. The values of  $M_{\text{site}}$  and  $M_{\text{cl}}$  can be determined experimentally from a combination of solid-state  $^{13}\text{C}$  NMR measurements and elemental analysis, as follows:

$$M_{\text{site}} = C_{\text{cl}} \left[ 12.01 \left( 1 - \frac{f_{\text{a}}^{\text{H}}}{f_{\text{a}}'} \right) + 13.02 \left( 1 - \frac{f_{\text{a}}^{\text{H}}}{f_{\text{a}}'} \right) \right] \quad (2)$$

$$M_{\text{cl}} = \frac{C_{\text{cl}} 12.01}{f_{\text{a}}' Y_{\text{C}}} \quad (3)$$

where  $C_{\text{cl}}$  is the number of aromatic carbons per cluster,  $f_{\text{a}}^{\text{H}}$  is the fraction of carbon which is aromatic and protonated,  $f_{\text{a}}'$  is the fraction of carbon that is aromatic, and  $Y_{\text{C}}$  is the daf mass fraction of carbon in the sample. Values of  $C_{\text{cl}}$ ,  $f_{\text{a}}^{\text{H}}$ , and  $f_{\text{a}}'$  have been determined for chars collected at various stages of pyrolysis.<sup>20,22</sup>  $N_{\text{site}}$  is defined on a per-aromatic-mass basis because aromatic mass per cluster in the char is fairly stable during rapid primary pyrolysis, remaining essentially unchanged

**Table 1. Properties<sup>a</sup> of Coals Used in Drop Tube Experiments by Perry<sup>20,22</sup>**

coal	$Y_{\text{C}}$	$Y_{\text{N}}$	$f_{\text{a}}'$	$f_{\text{a}}^{\text{H}}$	$C_{\text{cl}}$	$M_{\text{cl}}$	$M_{\text{site}}$	$N_{\text{site}}$
Yallourn	0.653	0.0052	0.57	0.16	14	452	172	0.0137
South Banko	0.714	0.0118	0.54	0.17	13	405	160	0.0298
Taiheyo	0.767	0.0113	0.51	0.16	14	430	173	0.0282
Miike	0.799	0.0118	0.64	0.22	14	329	173	0.0224
Hunter Valley	0.827	0.0208	0.71	0.25	13	266	161	0.0344
Pittsburgh	0.829	0.0164	0.70	0.27	15	311	186	0.0274
Upper Freeport	0.842	0.0155	0.81	0.28	18	317	222	0.0221
Pocahontas	0.916	0.0136	0.86	0.33	20	305	248	0.0167

<sup>a</sup>  $Y_{\text{C}}$  = daf mass fraction of carbon,  $Y_{\text{N}}$  = daf mass fraction of nitrogen,  $f_{\text{a}}'$  = carbon aromaticity,  $f_{\text{a}}^{\text{H}}$  = aromatic carbons with proton attachments,  $C_{\text{cl}}$  = aromatic carbons per cluster,  $M_{\text{cl}}$  = total mass per cluster,  $M_{\text{site}}$  = mass per cluster associated with aromatic portion, and  $N_{\text{site}}$  = mass of nitrogen per mass of aromatic portion of cluster.

**Table 2. Properties<sup>a</sup> of Chars from Drop Tube Experiments at 1100 K (Perry<sup>20,22</sup>)**

coal	$Y_{\text{C},0}$	$Y_{\text{N}}$	$f_{\text{a}}'$	$f_{\text{a}}^{\text{H}}$	$C_{\text{cl}}$	$M_{\text{cl}}$	$M_{\text{site}}$	$N_{\text{site}}$
Yallourn	0.653	0.0070	0.91	0.37	14	211	174	0.0085
South Banko	0.714	0.0158	0.91	0.34	16	251	198	0.0200
Taiheyo	0.767	0.0149	0.94	0.33	19	285	235	0.0181
Miike	0.799	0.0140	0.88	0.30	13	197	161	0.0172
Hunter Valley	0.827	0.0248	0.91	0.34	17.5	257	217	0.0294
Pittsburgh	0.829	0.0178	0.92	0.40	14	208	174	0.0212
Upper Freeport	0.842	0.0169	0.93	0.33	18	261	223	0.0198
Pocahontas	0.916	0.0142	0.95	0.36	19	260	235	0.0157

<sup>a</sup> See caption to Table 1.  $Y_{\text{C},0}$  = daf mass fraction of carbon in parent coal. Residence times were 234 ms.

during both tar release and light gas release. The value of  $N_{\text{site}}$  for the example cluster in Figure 2 is 14/177 or 0.079 (the same value is reached if eq 1 is used). Because nitrogen is a relatively small fraction of the total aromatic mass (usually less than 3%), light gas nitrogen release is assumed to have no significant effect on the aromatic mass per cluster.

The reported values of  $M_{\text{cl}}$  from the NMR analysis include cumulative errors from the all of the other measurements, such as  $f_{\text{a}}'$ ,  $C_{\text{cl}}$ , and  $Y_{\text{C}}$ . To reduce the small amount of scatter in the reported values of  $M_{\text{cl}}$ , Perry<sup>20</sup> normalized the values of  $M_{\text{cl}}$  in the char by the ratio of the reported values of  $M_{\text{site}}$  in the char and coal as follows:

$$(M_{\text{cl, char}})_{\text{adjusted}} = M_{\text{cl, char}} \left( \frac{M_{\text{site, coal}}}{M_{\text{site, char}}} \right) \quad (4)$$

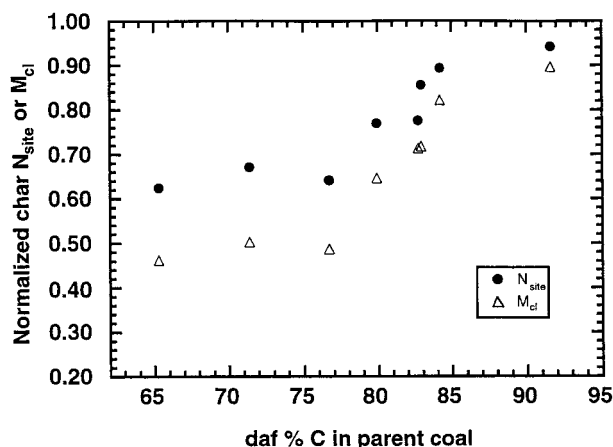
The ratio of  $M_{\text{site}}$  in the char to  $M_{\text{site}}$  in the coal should theoretically be unity at the heating rates considered here, and hence, this small correction helps focus comparisons on real effects rather than data scatter.

The measured values of the nitrogen in the tar, the nitrogen in the char, and the chemical structure data in the char ( $M_{\text{cl}}$ ,  $M_{\text{site}}$ , and  $N_{\text{site}}$ ) comprise a stringent test for any nitrogen evolution model. Such models must match not only the gas-phase nitrogen release but also the changes in the form of nitrogen in the char on a per cluster basis.

**Chemical Structural Relationships.** Several sets of char  $^{13}\text{C}$  NMR data were analyzed to identify relationships between char chemical structure and measured char  $N_{\text{site}}$  values. A summary of the data on coals and chars from pyrolysis experiments in a drop tube reactor at 1100 K in  $\text{N}_2$  by Perry<sup>20,22</sup> is shown in Tables 1 and 2. A strong correlation between  $N_{\text{site}}$  and

(22) Perry, S. T.; Hambly, E. M.; Fletcher, T. H.; Solum, M. S.; Pugmire, R. J. *Proc. Combust. Inst.* **2000**, 28, in press.



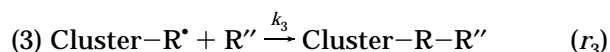
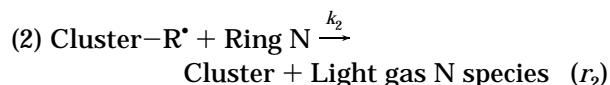


**Figure 3.** Comparison of the trend with rank for char nitrogen mass per aromatic mass ( $N_{\text{site}}$ ) and char molecular weight per cluster ( $M_{\text{cl}}$ ) values normalized to parent coal values for data reported by Perry and co-workers.<sup>22</sup> Chars were generated in drop tube pyrolysis experiments at 1100 K and 234 ms.  $M_{\text{cl}}$  values were adjusted according to eq 4. Carbon content is used as an indicator of rank.

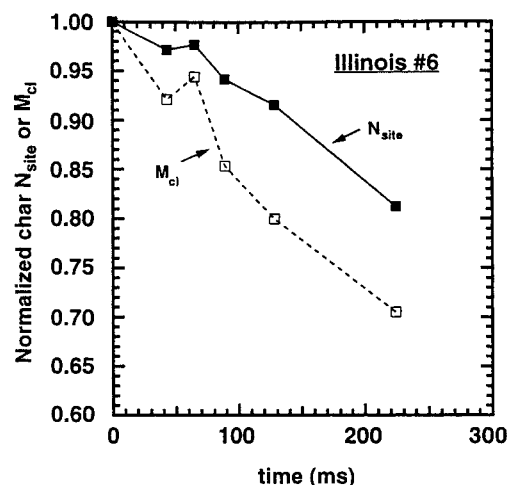
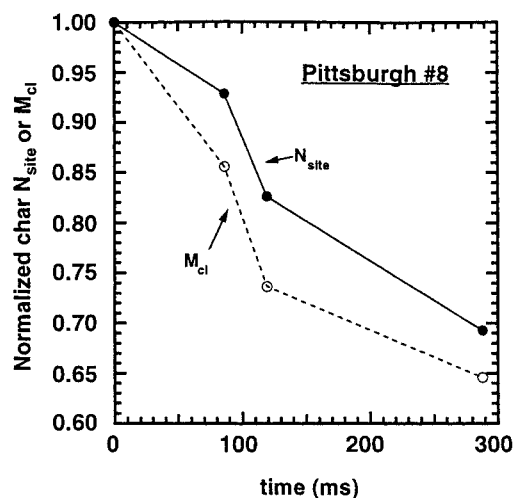
$M_{\text{cl}}$  in partially devolatilized chars from parent coals of a wide range of rank was observed, as shown in Figure 3, suggesting that they might share common chemistry. Although  $N_{\text{site}}$  and  $M_{\text{cl}}$  show nearly identical trends with rank, the difference between them also shows a clear trend with rank. For the conditions of this pyrolysis test, the gap between  $M_{\text{cl}}$  and  $N_{\text{site}}$  narrows as coal rank increases.

Other evidence for a strong relationship between  $N_{\text{site}}$  and  $M_{\text{cl}}$  is found in pyrolysis tests performed at Sandia in a drop tube with a 1250 K maximum gas temperature.<sup>23</sup>  $N_{\text{site}}$  and  $M_{\text{cl}}$  values for chars from two of the coals in the Sandia study are shown in Figure 4. Just as was seen in Figure 3, char values of  $N_{\text{site}}$  and  $M_{\text{cl}}$  follow the same trend, again implying a relationship between the two variables. Note that, even though Illinois No. 6 (hvCb) is of a lower rank than Pittsburgh No. 8 (hvAb), it shows less  $N_{\text{site}}$  decay at this condition than does Pittsburgh No. 8, which is in disagreement with the overall trend with rank seen in Figure 3. However, Illinois No. 6 also shows significantly less  $M_{\text{cl}}$  decay than Pittsburgh No. 8, consistent with the idea that  $N_{\text{site}}$  and  $M_{\text{cl}}$  share common chemistry.

**Fast Light Gas Nitrogen.** A three-step global mechanism for fast light gas nitrogen release (mechanism B above), consistent with the relationship between  $N_{\text{site}}$  and  $M_{\text{cl}}$ , is postulated as follows:



where Cluster-R-R' and Cluster-R-R'' are char (or coal) clusters with various aliphatic attachments,

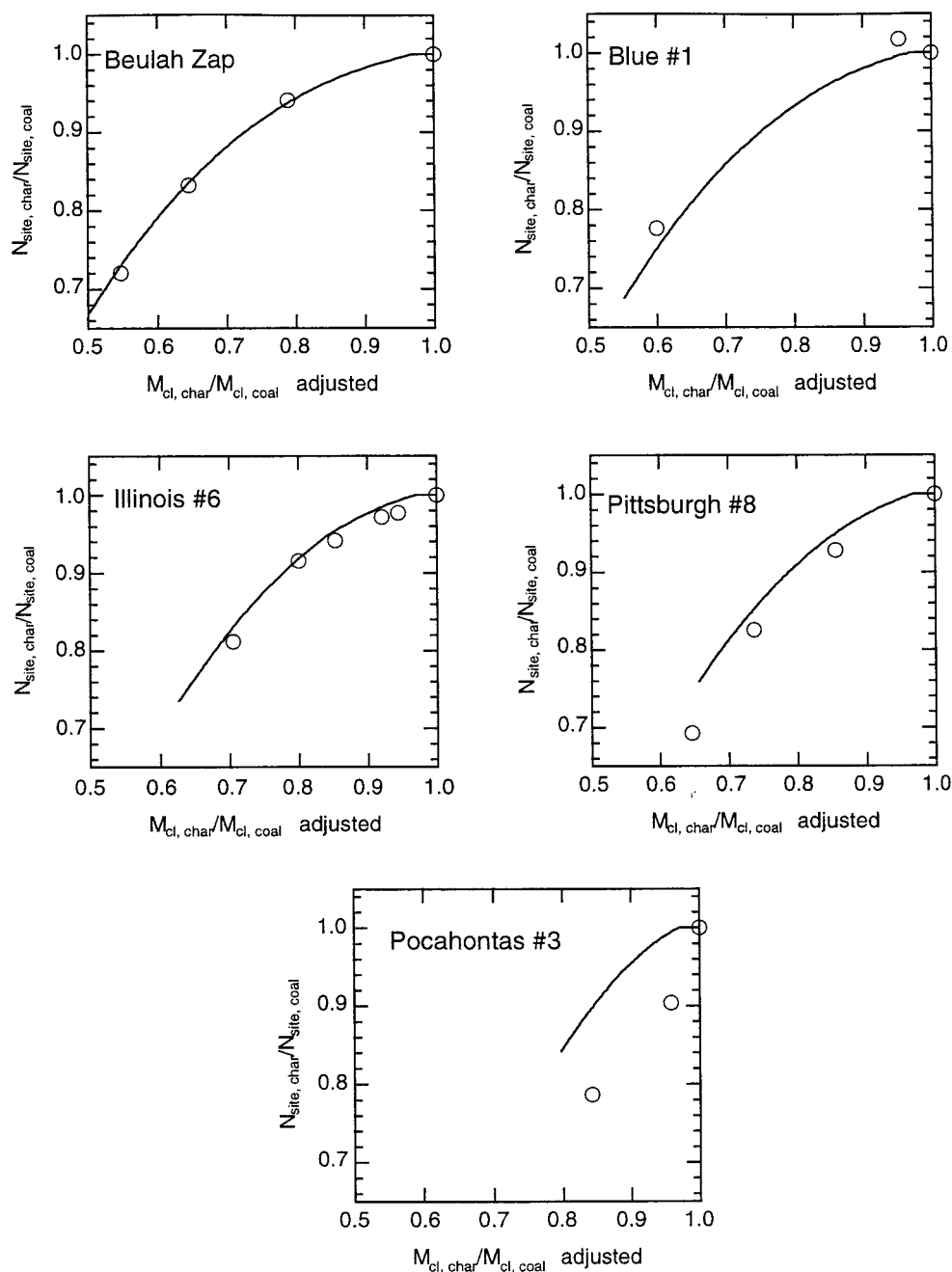


**Figure 4.** Comparison of the trend with pyrolysis time for measured char nitrogen mass per aromatic mass ( $N_{\text{site}}$ ) and measured char molecular weight per cluster ( $M_{\text{cl}}$ ) values normalized to parent coal values. Char data are from drop tube pyrolysis experiments performed at Sandia at 1250 K.<sup>23</sup>  $M_{\text{cl}}$  values were adjusted according to eq 4.

Cluster-R' is a free radical formed within the char matrix, 'R' is a light gas precursor that is also a free radical, Ring N is nitrogen contained within the aromatic portion of the char, and R'' is any material in the char that competes with Ring N for char free radicals. Steps 2 and 3 in this mechanism are not formal reactions. Additional free-radical products or reactants (not shown) must be involved in order to either conserve or terminate (via reaction with another free radical) the unpaired electron found in each of these reactions. Thus, it should be assumed, although not specifically shown, that additional free radicals are formed as gas-phase products in steps 2 and 3 and released as light gas precursors.

Some initial fraction of char free radicals may build up and still be stabilized by resonance throughout the char network. However, once the cluster is saturated, any new radicals formed via step 1 will be reactive (unstable). At that point, steps 2 and 3 compete for the unstable char free radicals thus formed. Step 3 is ageneral solid-phase free-radical reaction/stabilization step, which occurs very quickly and probably includes thousands of specific reactions, including hydrogenation,

(23) Fletcher, T. H.; Hardesty, D. R. *Milestone Report for DOE's Pittsburgh Energy Technology Center*; Contract FWP 0709; Sandia Report No. SAND92-8209; Sandia National Laboratory: Albuquerque, NM, 1992. Available via NTIS (<http://www.ntis.gov>).



**Figure 5.** Predicted decay (lines) of  $N_{\text{site}}$  compared to values calculated from measured chemical structural data (symbols) published by Fletcher and Hardesty<sup>23</sup> for drop tube pyrolysis of five coals at 1250 K maximum gas temperature and 250–300 ms residence time. Char  $M_{\text{cl}}$  values are adjusted for changes in measured  $M_{\text{site}}$  values (see eq 4).

char bridge formation, cross-linking, etc. Thus, the rate of reaction of ring nitrogen depends inversely on the concentration of material available to react with free radicals via step 3.

Light gas nitrogen formation due to tar secondary reactions is not modeled by this mechanism. There are two reasons for this: (1)  $N_{\text{site}}$  decay was shown to be more severe in chars than in tars during primary pyrolysis;<sup>20</sup> and (2) a large proportion of the nitrogen is lost from the tar during soot formation,<sup>24,25</sup> a process that is not yet well understood.

A rate equation was developed from this global mechanism to model the rate of fast light gas nitrogen release, as outlined below. The rate of disappearance of ring nitrogen is the rate of step 2 ( $r_2$ )

$$-\frac{d[\text{ring N}]}{dt} = r_2 = k_2[\text{Cluster-R}'][\text{ring N}] \quad (5)$$

where the square brackets denote concentration (grams per gram of aromatic material). Assuming the steady-

(24) Chen, J. C.; Niksa, S. *Twenty-Fourth Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1992; pp 1269–1276.

(25) Rigby, J. R. Experimentally Determined Optical Properties and Chemical Compositions of Coal-Derived Soot. Ph.D. Dissertation (Mechanical Engineering), Brigham Young University, Provo, UT, 1996.

state approximation for *unstable* cluster free radicals and assuming that the rate of step 2 is negligible relative to the rate of step 3, a simple expression for [Cluster-R•] is obtained, which can be substituted into eq 5 to give

$$-\frac{d[\text{ring N}]}{dt} = k_2 \left\{ \frac{r_1}{k_3 [\text{R}'']} \right\} [\text{ring N}] = \frac{k_2}{k_1} \left\{ \frac{r_1}{[\text{R}'']} \right\} [\text{ring N}] \quad (6)$$

where  $k_2$  and  $k_3$  are the Arrhenius rate constants for steps 2 and 3, respectively.

This rate equation predicts that once unstable char radicals begin to form, the rate of ring nitrogen decay should be proportional (a) to the concentration of ring nitrogen and (b) to the overall rate of light gas release ( $r_1$ ). The rate of light gas formation ( $r_1$ ) can be defined as the negative fractional change in the molecular weight per cluster as follows:

$$r_1 = \frac{-1}{M_{\text{cl}}} \frac{d(M_{\text{cl}})}{dt} \quad (7)$$

The ring nitrogen concentration is defined as  $N_{\text{site}}$ , and it is assumed that  $[\text{R}'']$  is proportional to the average total mass per cluster ( $M_{\text{cl}}$ ). Because  $[\text{R}'']$  competes with  $N_{\text{site}}$  for free radicals, it must be expressed on the same basis as  $N_{\text{site}}$ , that is, per average aromatic mass per cluster as follows:

$$[\text{R}''] = \frac{M_{\text{cl}}}{M_{\text{site}}} \quad (8)$$

Substituting the above definitions and assumptions into eq 6 and substituting a single rate constant for the ratio of the rate constants of steps 2 and 3 gives the final rate equation

$$\frac{d(N_{\text{site}})}{dt} = A_N \exp\left(\frac{-E_N}{RT_p}\right) \frac{M_{\text{site}}}{(M_{\text{cl}})^2} \frac{d(M_{\text{cl}})}{dt} N_{\text{site}} \quad (9)$$

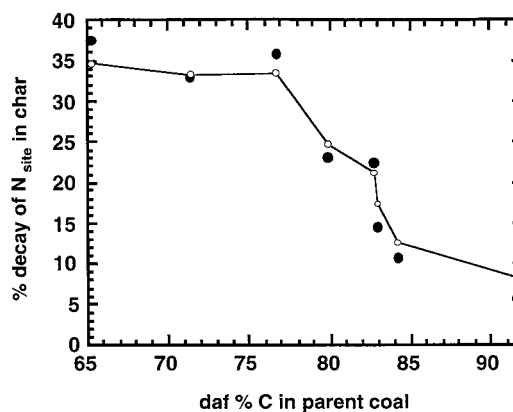
where  $A_N$  and  $E_N$  are the preexponential factor and activation energy, respectively, for fast light gas nitrogen release;  $R$  is the universal gas constant; and  $T_p$  is the particle temperature.

An empirical parameter,  $f_{\text{stable}}$ , was used to represent the initial fraction of decay in  $M_{\text{cl}}$  that occurs before  $N_{\text{site}}$  is allowed to decay. Thus, the use of  $f_{\text{stable}}$  allows an initial fraction of *stable* free radicals to build up in the char, which does not cause any nitrogen release via ring rupture.

**Slow Light Gas Nitrogen.** Slow light gas nitrogen release is assumed to be first-order in  $N_{\text{site}}$  as follows:

$$\frac{-d(N_{\text{site}})}{dt} = A_4 \exp\left(\frac{-E_4}{RT_p}\right) N_{\text{site}} \quad (10)$$

Although slow light gas nitrogen release can be modeled using a distributed activation energy, the additional complexity does not seem justified because of the lack



**Figure 6.** Trend with rank of measured (symbols) and predicted (line)  $N_{\text{site}}$  decay for chars produced by Perry in a drop tube at 1100 K and 234 ms.<sup>22</sup> Parent coal carbon content is used as an indicator of rank.

of detailed long-residence-time high-temperature pyrolysis data.

**Model Parameters.** For the fast light gas nitrogen release portion of the model, measured char  $M_{\text{cl}}$  and  $N_{\text{site}}$  values were used to regress appropriate values for the preexponential factor ( $A_N$ ) and activation energy ( $E_N$ ). Data sets were therefore used that included  $^{13}\text{C}$  NMR analyses of chars as well as elemental analyses. This regression was performed using data published by Fletcher and Hardesty<sup>23</sup> for (a) experiments performed at 1250 K (~300 ms) and 1600 K (~40 ms) and (b) data reported by Perry et al.<sup>22</sup> for drop tube pyrolysis of eight coals at 1100 K (~240 ms), because  $^{13}\text{C}$  NMR chemical structural data were available for both of these tests. It was found that the data could be fit fairly well using values of  $A_N = 18.4$  (unitless) and  $E_N = 6$  kcal/mol (see Figures 5 and 6). The relatively low apparent activation energy is not unreasonable because it represents the *difference* between the activation energies of competing steps 2 and 3 of the free-radical mechanism.

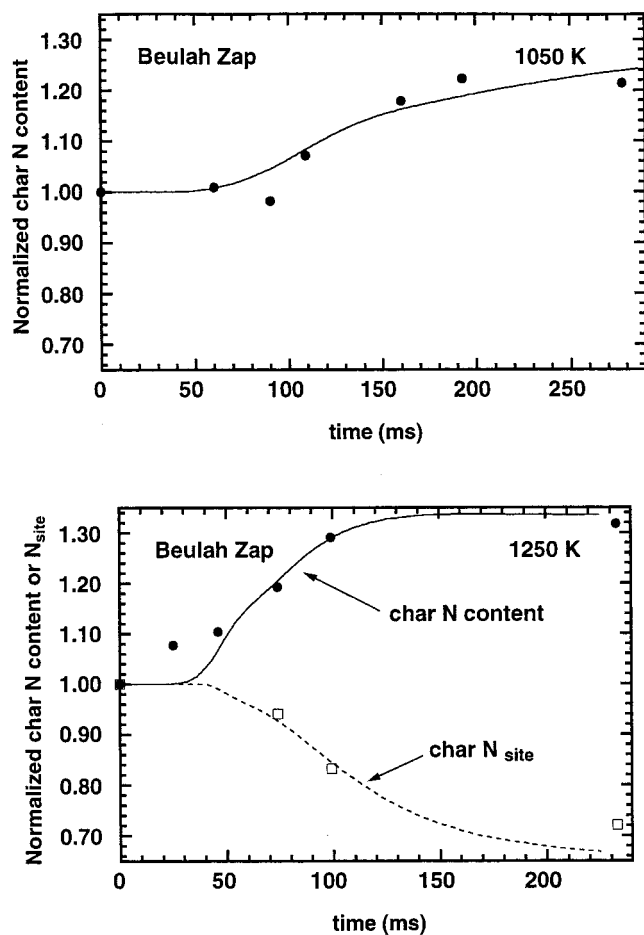
It was assumed that the radicals formed during the initial 3% of light gas release were stable (i.e.,  $f_{\text{stable}} = 0.03$ ). This means that  $N_{\text{site}}$  was assumed to remain at the value in the parent coal until the molecular weight per cluster had decayed to 97% of the coal value. It is not clear whether this empiricism is really necessary, although it seems to fit the available data for high-rank coals somewhat better than using  $f_{\text{stable}} = 0$ , consistent with the concept of the formation of a pool of free radicals before steady state is reached.

## Results and Discussion

Comparisons of predicted and measured  $M_{\text{cl}}$  and  $N_{\text{site}}$  are shown in Figure 5 for chars produced in a drop tube<sup>23</sup> with a maximum gas temperature of 1250 K quenched at various points along the pyrolysis path. Char values for  $M_{\text{cl}}$  and  $N_{\text{site}}$  are normalized to the parent coal values for ease of comparison. For the data shown in Figure 5, it appears that the higher the coal rank, the more steep the slope of  $N_{\text{site}}$  decay, a trend that is correctly predicted by the light gas nitro-

(26) Smith, K. L.; Smoot, L. D.; Fletcher, T. H.; Pugmire, R. J. *The Structure and Reaction Processes of Coal*; Plenum Press: New York, 1994.

(27) Genetti, D. B. An Advanced Model of Coal Devolatilization Based on Chemical Structure. M.S. Thesis (Chemical Engineering), Brigham Young University, Provo, UT, 1999.



**Figure 7.** Comparison of predicted and measured char nitrogen content and char  $N_{\text{site}}$  value for a North Dakota lignite pyrolyzed in a drop tube reactor with 1050 K (upper graph) and 1250 K (lower graph) maximum gas temperatures at Sandia.<sup>23</sup> Nitrogen values are normalized to parent coal nitrogen values. Predictions made using measured parent coal  $^{13}\text{C}$  NMR structural parameters.

gen mechanism. In Figure 6, predicted values of  $N_{\text{site}}$  are compared with experimental data reported by Perry et al.<sup>22</sup> for drop tube tests performed at 1100 K ( $\sim 240$  ms). The predicted points are connected by a line for illustration purposes only. Using no coal-dependent parameters other than  $^{13}\text{C}$  NMR measurements of the parent coal chemical structure, the nitrogen model using the free-radical mechanism gives predicted  $N_{\text{site}}$  values that follow the rank trend of the data in Figure 6 very well.

Another method for evaluating the performance of the free-radical-based nitrogen model for light gas release is to compare predicted and measured values of daf char nitrogen content. In Figure 7, predictions of changes in daf char nitrogen content and  $N_{\text{site}}$  (normalized to the parent coal values) as a function of pyrolysis residence time show good agreement with measured values for a North Dakota lignite pyrolyzed in a drop tube at Sandia at 1050 and 1250 K. Predicted daf nitrogen contents also show good agreement with pyrolysis test data for chars from eight coals produced by Perry et al.<sup>22</sup> in a drop tube ( $\sim 10^4$  K/s) at 900, 1000, 1100, and 1250 K, and in a flat flame reactor ( $\sim 10^5$  K/s) at 1650 K (see Figure 8). In Figure 8, char nitrogen mass fractions have

been normalized to the parent coal value to provide a more stringent comparison and to better show trends with rank.

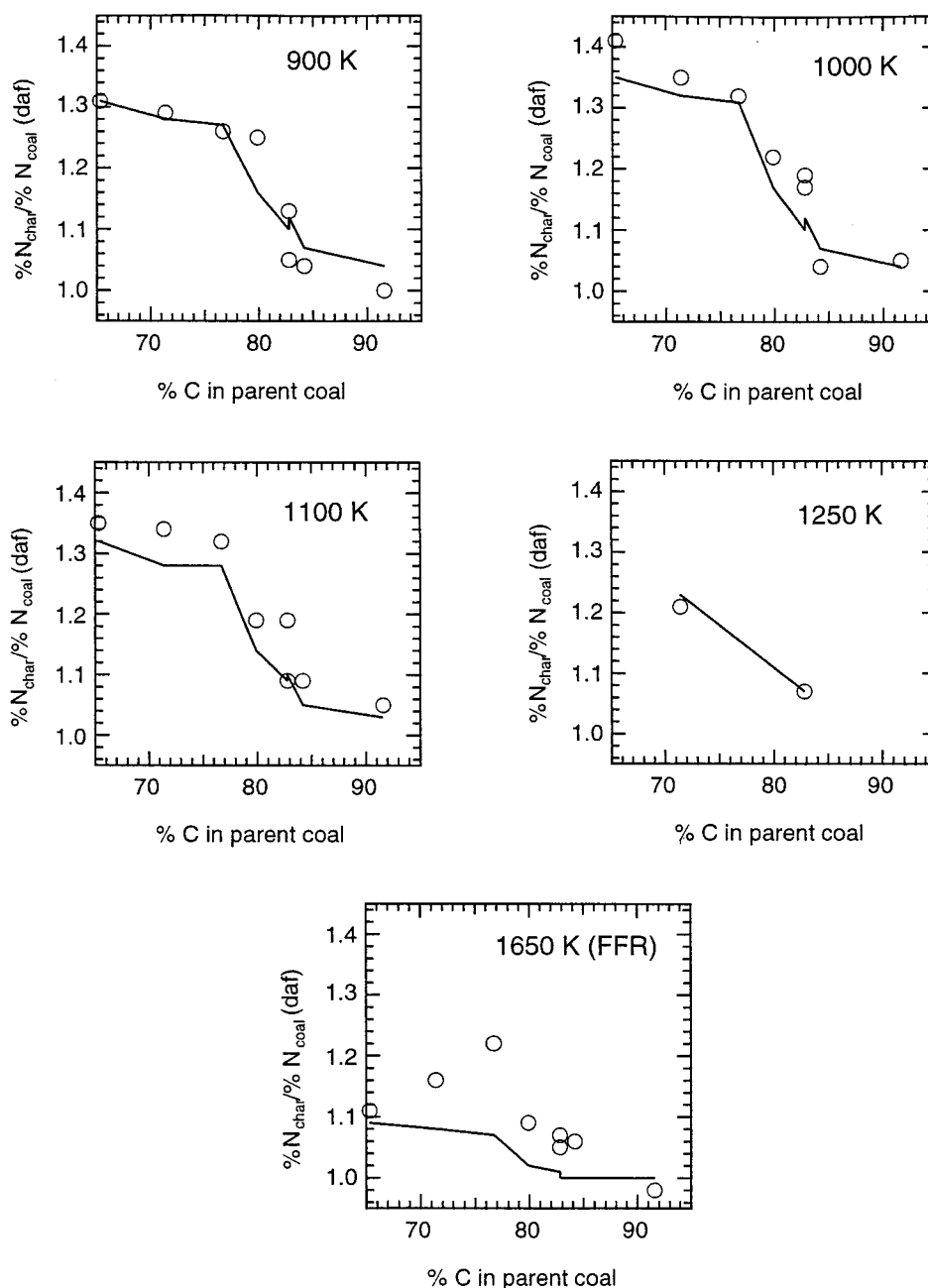
The performance of the free-radical-based light gas nitrogen release mechanism was also evaluated against a variety of data not used in the model development. Examples of these are shown in Figures 9 and 10, which show good agreement between nitrogen model predictions and experimental data for pyrolysis of coals at low (0.5 K/s) and high ( $10^5$  K/s) heating rates, respectively.

Very few data are available for evaluation of the mechanism for slow light gas release. The slow nitrogen release step (eq 10) was initially assumed to have an activation energy of 70 kcal/mol, which is similar to the results of Mackie et al.<sup>15</sup> Data from Blair and Wendt<sup>18</sup> for pyrolysis of an Illinois No. 6 coal on a graphite ribbon at 2000 K for about 2 s was used to fit the preexponential factor for the slow nitrogen release step at  $5.5 \times 10^7 \text{ s}^{-1}$ . It is likely that these rate expression parameters somewhat overpredict nitrogen release during severe, long-residence-time pyrolysis as 99% nitrogen release is predicted after only 2.5 min at 2100 K, whereas Pohl and Sarofim<sup>17</sup> reported that 20 min at 2100 K may be necessary to achieve complete nitrogen release. The predicted slow light gas nitrogen release is not significant compared to the overall nitrogen release for conditions encountered in pulverized-coal combustors but may be important in fixed-bed or fluidized conditions.

A comparison with the Pittsburgh No. 8 data of Pohl and Sarofim<sup>17</sup> was made, assuming a heating rate of 1 K/s, a hold time of 20 min at each temperature, and a cooling ramp of 20 min. Actual hold times used in the experiment at each temperature were not well documented; some of the hold times in the experiment may have been as long as 1.5 h. Because NMR data were available for a similar Pittsburgh No. 8 coal, no adjustable parameters were used. Results presented in Figure 11a show that the mass release predictions were in good agreement with the data. The nitrogen release from the char was in fair agreement with the limited data from Pohl and Sarofim, showing complete nitrogen release at about 2000 K, with a large gap in the data in the region of 1300–1500 K.

To provide more nitrogen release data in the 1300–1500 K region, three char samples were made by heating 0.7–0.8 g of a Pittsburgh No. 8 coal in a ceramic crucible to the desired temperature at 1 K/s in a furnace flooded with  $\text{N}_2$ , with a 20 min hold time at the desired temperature. Cooling rates were approximately 1 K/s. Elemental analysis was performed by Galbraith Laboratories. Results of these experiments are also plotted in Figure 11a. The mass release for these BYU experiments was slightly higher than that observed by Pohl and Sarofim, possibly because of slight differences in coal type. Figure 11a shows that the range of activation energies chosen (70–80 kcal/mol) for the slow nitrogen release step was appropriate, but that the shape of the predicted curve did not seem to match the data very well. A distributed activation energy was therefore used for the slow light gas nitrogen step, with a mean activation energy of 75 kcal/mol, the same preexponential factor ( $5.5 \times 10^7 \text{ s}^{-1}$ ), and a standard deviation in the activation energy ( $\sigma_{\text{EA}}$ ) of 3 kcal/mol. The prediction





**Figure 8.** Predicted (lines) and measured (symbols) values of char nitrogen content normalized to the parent coal nitrogen content for drop tube and flat flame reactor pyrolysis experiments of Perry and co-workers.<sup>22</sup> Carbon content is used as an indicator of rank.

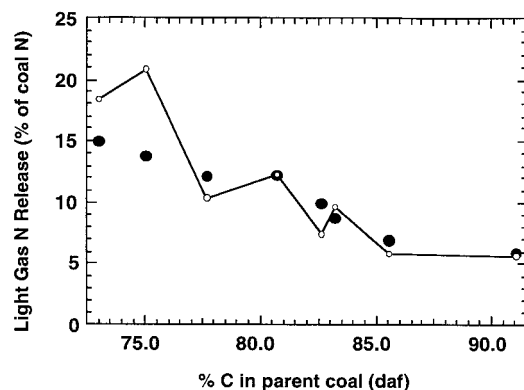
made using the distributed activation energy model is shown in Figure 11b. The distributed activation energy model seems to match the shape of the nitrogen release data much better than the simple first-order expression with a constant activation energy. The justification for using a distributed activation energy is that the more stable nitrogen forms require a higher temperature for decomposition; hence, the effective activation energy changes slightly as the less stable nitrogen forms are depleted in the char.

The rate parameters used in these predictions are summarized in Table 3. It should be noted that the slow light gas nitrogen step (eq 10, including the last three parameters in Table 3) may not be needed for typical entrained flow pyrolysis predictions, as this reaction

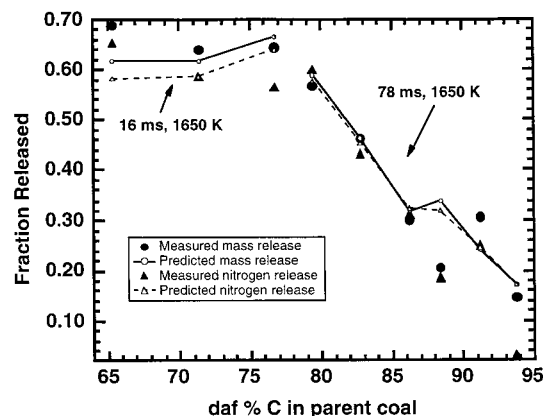
**Table 3. Summary of Free-Radical Mechanism Parameters as Used in This Study**

$A_N$ (fast light gas)	18.4 (unitless)
$E_N$ (fast light gas)	6.0 kcal/mol
$f_{\text{stable}}$ (fraction of $M_{\text{cl}}$ decay with no $N_{\text{site}}$ decay)	0.03
$A_4$ (slow light gas)	$5.5 \times 10^7 \text{ s}^{-1}$
$E_4$ (slow light gas)	75 kcal/mol
$\sigma_{E4}$ (standard deviation of $E_4$ )	3 kcal/mol

only becomes significant at elevated temperatures (> 1300 K) and long residence times (on the order of minutes even at 1700 K). It is anticipated that more refinements could be made to the values of the high-temperature, slow light gas nitrogen rate coefficients if additional data were available.



**Figure 9.** Comparison of predicted (lines) total light gas nitrogen yields with the measured (points) HCN + NH<sub>3</sub> yields reported by Basilakis et al.<sup>6</sup> for 0.5 K/s pyrolysis of the Argonne premium coals with a maximum particle temperature of 1173 K and a hold time of 3 min. Predictions made using parent coal <sup>13</sup>C NMR structural parameters reported by Smith et al.<sup>26</sup>

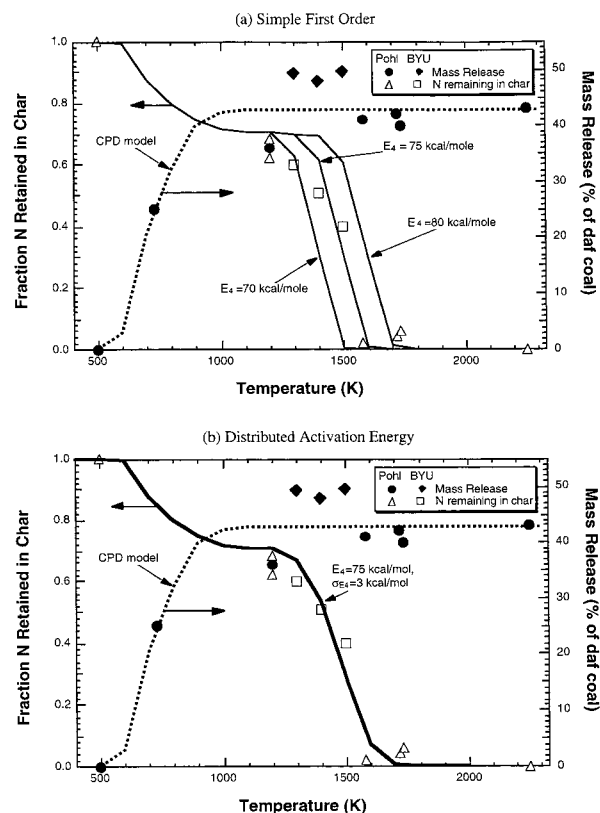


**Figure 10.** Comparison of predicted total mass and nitrogen release values with measured values reported by Perry<sup>20</sup> and Genetti<sup>27</sup> for flat flame reactor pyrolysis experiments at 1650 K.

### Conclusions

A global mechanism for (fast) light gas nitrogen release during coal devolatilization was developed, and a corresponding rate expression was derived. This rate equation was used together with a first-order (slow) light gas nitrogen release rate equation to predict light gas nitrogen variations with time, temperature, heating rate, and coal rank, based only on six coal-independent rate constants, the transient particle temperature profile, and the transient char cluster molecular weight. These light gas nitrogen release rate equations were incorporated into an existing nitrogen release model, which included nitrogen release with the tar. Model predictions showed good agreement with experimental pyrolysis data for a wide range of heating rates, temperatures, residence times, and coal types.

The free-radical-based nitrogen model is the first to describe the rank dependence of nitrogen release as



**Figure 11.** Comparison of model predictions with crucible data for a Pittsburgh No. 8 coal from Pohl and Sarofim<sup>17</sup> and from BYU (1 K/s, 20 min hold at each temperature, and 20 min cool). (a) Effect of activation energy using a simple first-order rate expression for the high-temperature nitrogen release with  $A = 5.5 \times 10^7 \text{ s}^{-1}$ . (b) Reasonable agreement using a distributed activation energy rate expression with  $A = 5.5 \times 10^7 \text{ s}^{-1}$ ,  $E_{\text{mean}} = 75 \text{ kcal/mol}$ , and  $E_g = 3 \text{ kcal/mol}$ .

light gas without the use of correlations. The free-radical mechanism also offers reasonable explanations for the observed release of ring nitrogen at relatively low temperatures and for the inherent stability of much of the char nitrogen during pyrolysis, observations not easily explained by a simple thermal decomposition model alone.

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