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**SENSITIVITY ANALYSIS OF A REACTION MODEL
FOR THE RADIATION TREATMENT OF COMBUSTION GASES**

**ANALYSE DE SENSIBILITÉ D'UN MODÈLE DE RÉACTION POUR
LE TRAITEMENT DES GAZ DE COMBUSTION PAR RAYONNEMENT**

L. W. Dickson, J. Paquette, F. Busi, M. D'Angelantonio

Whiteshell Laboratories

Laboratoires de Whiteshell

Pinawa, Manitoba R0E 1L0

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by

L.W. Dickson,¹ J. Paquette,¹ F. Busi^{2,3} and M. D'Angelantonio³

1. Current address: Chalk River Laboratories, Chalk River, Ontario
K0J 1J0
2. Istituto Scienze Chimiche, Universita di Bologna, Bologna, Italy
3. Istituto di Fotochimica e Radiazioni d'Alta Energia del C.N.R., Bologna,
Italy

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Pinawa, Manitoba ROE 1L0
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RÉSUMÉ

On a effectué des analyses de sensibilité de mécanismes chimiques pour le traitement des gaz de combustion par rayonnement de haute énergie. L'analyse de sensibilité des réactions de production de radicaux a montré que la concentration de radicaux ne dépend pas fortement des vitesses de réaction de molécules ioniques. On a réalisé un modèle simplifié de production de radicaux d'après ce résultat. Des analyses de sensibilité de mécanismes d'enlèvement de NO_x et de NO_x/SO_2 ont montré que la plupart des réactions biradicalaires pourraient être éliminées de ces mécanismes sans influencer les concentrations importantes prédites d'espèces. Les résultats des analyses de sensibilité ont fourni une indication utile pour la réduction du modèle mais il a fallu certaines connaissances chimiques pour interpréter correctement les conséquences de l'analyse de sensibilité.

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ABSTRACT

Sensitivity analyses were performed on chemical mechanisms for the treatment of combustion flue gases with high-energy radiation. The sensitivity analysis of the radical production reactions showed that the radical concentrations did not depend strongly on most of the ion-molecule reaction rates. A simplified radical production model was developed based on this result. Sensitivity analyses performed on the NO_x and NO_x/SO_2 removal mechanisms showed that most of the radical-radical reactions could be removed from these mechanisms without affecting the predicted major species concentrations. The sensitivity analysis results provided a useful guide for model reduction, but some chemical knowledge was also required to interpret the implications of the sensitivity analysis correctly.

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CONTENTS

	<u>Page</u>
1. INTRODUCTION	1
2. REACTION MECHANISM	2
3. COMPUTATIONAL METHOD	3
4. RESULTS AND DISCUSSION	4
5. CONCLUSIONS	8
REFERENCES	8
TABLES	11
FIGURES	24

1. INTRODUCTION

The contribution of nitrogen oxide and sulphur dioxide by-products from fossil fuel combustion to the "acid rain" problem has received worldwide attention in recent years [1,2]. Many of the existing processes for the control of these by-product emissions from stationary sources suffer from economic or technological limitations [3,4]. Hence, research into alternative processes with potential for reducing NO_x and SO₂ emissions from fossil-fuel-fired power plants continues.

New combustion flue gas cleaning processes based on radiation treatment with high-energy electron beams appear to have potential for simultaneous control of both NO_x and SO₂ emissions [5-11]. The underlying chemistry of these processes has been studied extensively [12,13] and several process chemistry models have been formulated [13-20]. The model developed by Busi and co-workers [17-19] is based on primary ion and radical yields from the radiation chemistry literature [21] and chemical reaction rates from atmospheric chemistry studies [22-26]. The dose dependence of the NO, NO₂ and SO₂ concentrations given by this model are in good agreement with experimental results. However, some of the species that this model predicts to be major products, e.g., H₂SO₅ and HSO₅N, may not be the final products collected in the condensed phase.

The advent of high-speed computers and more efficient algorithms has made it practical to perform sensitivity analyses on large chemical reaction sets [27,28]. A sensitivity analysis of a chemical reaction mechanism yields the dependence of species concentrations on input parameters, such as rate constants and initial concentrations. The dependence of product concentrations on reaction rate constants can be used to aid in identifying 1) reaction rate constants that need to be determined more accurately, and 2) unimportant reactions in a complex mechanism. The dependence of product concentrations on reactant concentrations can aid in optimizing product species profiles [29,30].

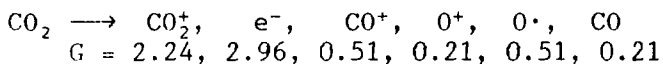
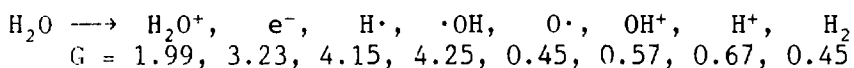
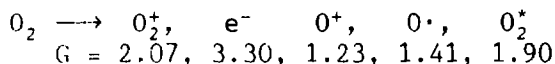
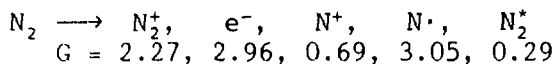
This paper presents the results of a sensitivity analysis of the radical production, NO_x oxidation [17], and NO_x/SO₂ oxidation [18] reaction mechanisms proposed for the radiation treatment of flue gases. The sensitivity coefficients, $d[i]/dk_j$, the partial derivative of the concentration of species *i* with respect to the rate constant for reaction *j*, were calculated for the major species in each reaction set. The calculated elementary sensitivity coefficients were converted to the normalized sensitivity coefficients,

$$\frac{d(\ln[i])}{d(\ln k_j)} = \frac{k_j}{[i]} \frac{d[i]}{dk_j} .$$

Chemical knowledge was used to determine which of the reactions in each set, with small normalized sensitivity coefficients, could be removed from the reaction set without affecting the predicted major species concentrations. The end result of this process was the identification of three simplified reaction models predicting major species concentrations that are in good agreement with those given by the corresponding full mechanisms over a wide range of conditions.

2. REACTION MECHANISM

The reaction mechanism for radiolytic oxidation of nitrogen oxides in a flue gas mixture with rate constants for a temperature of 25°C is given in Table 1 [17]. The rate constants for Reactions 1 to 15 in Table 1 were derived from the following radiation chemical yields (G-values in molecule·(100 eV)⁻¹ units):



The yields of primary species from radiolysis of H₂O and CO₂ have been changed slightly from the values in Reference 17 to satisfy charge and mass balance. A dose rate of 10 kGy·s⁻¹ (1 Mrad·s⁻¹) and a flue gas composition of 68.0% N₂, 15.5% O₂, 10.5% H₂O and 6.0% CO₂ were also used in the calculation of the rate constants of Reactions 1 to 15 in Table 1. Reactions 16 to 38 are ion-molecule and ion neutralization reactions. Overall radical yields of G(·OH) = 3.26, G(H·) = 3.34, G(N·) = 2.47, G(O·) = 0.68 and G(CO) = 0.24 are obtained from Reactions 1 to 38 in this gas mixture. Reactions 39 to 66 in Table 1 are reactions of nitrogen oxides and other inorganic compounds with rate constants appropriate for 25°C. The additional reactions required to model the radiolytic oxidation of sulphur dioxide and the rate constants for NO_x reactions at 120°C are presented in Table 2 [18]. The reactions of organic compounds included in Reference 17 have been neglected in the present study.

Sensitivity analyses have been performed on three reaction sets. A flue gas composition of 68.0% N₂, 15.5% O₂, 10.5% H₂O and 6.0% CO₂, and Reactions 1 to 38 (Table 1) were used for a sensitivity analysis of the radical yields in the system. Initial concentrations of 250 ppm* NO and 15 ppm NO₂ and Reactions 39 to 66 (Table 1) were added for a sensitivity analysis of the NO_x reaction mechanism at 25°C. Finally, a sensitivity analysis of the NO_x/SO₂ reaction mechanism at 120°C was performed by adding an initial concentration of 190 ppm SO₂ and the reactions and appropriate rate constants from Table 2 to the previous reaction set.

* 1 ppm = 1 µL/L

3. COMPUTATIONAL METHOD

The sensitivity coefficients were obtained using a modified version of the computer program described by Valko and Vadja [31]. The program uses a generalized Runge-Kutta method, of order four, with three function evaluations per step, to perform the numerical integration and an embedded third-order method to control step size. The method is A-stable and can handle stiff differential equations [32-34]. The sensitivity analysis is performed by the decomposed direct method, as originally described by Dickinson and Gelinas [35]. The algorithm described by Valko and Vadja was modified to implement relative error control as follows. The algorithm deems acceptable the values of Y (concentrations or sensitivities) computed over the current integration step, if the current estimate, Est, of the local truncation error in Y satisfies

$$\text{Est} < (\text{Tol})(\text{Ybase})$$

where Tol is the tolerable relative error and Ybase is related to Y. Relative error control was established using

$$\text{Ybase} = \max(\text{abs}(Y), \text{Ysig})$$

where Ysig is the significance level, that is, the value at which a variable may be assumed to be zero for all practical purposes. The significance level was set at $10^{-20} \text{ mol} \cdot \text{dm}^{-3}$ for the concentrations and at $10^{-25} \text{ mol}^2 \cdot \text{dm}^{-6} \cdot \text{s}$ for the sensitivity coefficients. The use of relative error control was found to significantly improve the performance of the algorithm. The tolerable relative error was set at 10^{-3} for both the concentrations and the sensitivities. The user interface was based on the one used in the program MAKSIM [36-38]. The performance of the integrator was checked by running test cases and comparing the output with the results obtained with the program MAKSIM. The test cases described by Carver and co-workers [39] were used. The sensitivity analysis part of the program was tested by running the cases described by Valko and Vadja. The accuracy of the calculated sensitivities was also checked using mass-balance considerations. Conservation of mass requires that

$$\sum (n_{im} d[i]/dk_j) = 0$$

where n_{im} is the number of atoms of m in species i and $d[i]/dk_j$ is the sensitivity coefficient for the dependence of the concentration of species i on the rate constant for reaction j. A test mass-balance calculation showed agreement to within $\pm 0.1\%$ of the largest sensitivity coefficient.

The sensitivity analysis computations were performed on a Floating Point Systems model M64/140 mini supercomputer under the G00 operating system level using the APMATH subroutine library. Most of the computer code was written in FORTRAN, but a few key subroutines were written in ASSEMBLY language to reduce the computation time. The sensitivity analysis calculation of the radical production mechanism to 1-s chemical time required about 0.1-h computation time. The calculations for the NO_x reaction mechanism to 5 s and for the NO_x/SO_2 reaction mechanism to 3 s required 11.4 and 30.1 h of computation time respectively.

4. RESULTS AND DISCUSSION

A sensitivity analysis of the radical production reactions (Reactions 1 to 38 in Table 1) was performed. The normalized sensitivity coefficients, $d(\ln[i])/d(\ln k_j)$, were calculated for $H\cdot$, $\cdot OH$, $N\cdot$, $O\cdot$ and CO at a time of 1.0 s (10-kGy dose). These values are shown in Table 3. Most of the normalized sensitivity coefficients for Reactions 1 to 15 are between 0.01 and 0.50 for radicals produced either directly in that reaction or indirectly from products of the reaction. In contrast, most of the normalized sensitivity coefficients for Reactions 16 to 38 are less than 10^{-5} , indicating that these reactions could potentially be eliminated in the formation of a reduced model. The insensitivity of radical concentrations to the rates of Reactions 16 to 38 is due to the relatively fast rates of the ion-molecule reactions compared with the rates of the initial species production reactions and, also, to the existence of few competitive reaction channels. This sensitivity information indicates that the radical production reaction mechanism may be simplified.

The competitive reaction channels that must be included in a simplified radical production model are denoted by reactions with relatively large and equal magnitude but opposite-sign normalized sensitivity coefficients. For example, $d(\ln[O\cdot])/d(\ln k_{20}) = -d(\ln[O\cdot])/d(\ln k_{38}) = 0.126$ indicates that the rate of dissociation of oxygen molecules by excited nitrogen molecules via Reaction 32 is comparable to, and competitive with, the rate of deactivation of excited nitrogen by oxygen molecules via Reaction 33. Since there are no other competitive reactions of N_2^* in the model, the two reactions are easily simplified as a reduced yield of N_2^* production. The normalized sensitivity coefficients

$$\frac{d(\ln[O\cdot])}{d(\ln k_{20})} = -\frac{d(\ln[O\cdot])}{d(\ln k_{38})} = 0.0645 \quad \text{and}$$

$$\frac{d(\ln[CO])}{d(\ln k_{20})} = -\frac{d(\ln[CO])}{d(\ln k_{38})} = -0.184$$

show a competition between reactions of O^+ with H_2O (Reaction 20) and CO_2 (Reaction 38). These competitive reactions must be included explicitly in a simplified model because the ratio of concentrations of H_2O and CO_2 is not always the same in different flue gas mixtures.

The reactions of the other ionic species produced in Reactions 1 to 15 may be simplified by assuming that the ion-molecule reactions are relatively fast and analyzing the reaction channels of each ion. For example, The N_2^+ produced in Reaction 1 may react with H_2O to produce H_2O^+ (Reaction 17) or with O_2 to produce O_2^+ (Reaction 22), which subsequently reacts with H_2O to produce H_2O^+ (reaction 19). The H_2O^+ reacts via Reactions 21, 24, 25 and 28, ultimately producing one $H\cdot$ atom and one $\cdot OH$ radical for each N_2^+ ion initially formed. A similar analysis of the reaction channels available to each of the other ionic species produced in Reactions 1 to 15, within the constraints of the competitive channels noted above, leads to the formulation of the simplified radical production model shown in Table 4.

This simplified radical production model gives $\cdot\text{OH}$, $\text{N}\cdot$, $\text{O}\cdot$ and CO radical concentrations at times of 10^{-3} to 1 s that are in excellent quantitative agreement with those predicted by the full mechanism (Reactions 1 to 38). The simplified model gives an $\text{H}\cdot$ atom concentration at early times (10^{-3} s) that is about a factor of two higher than that given by the detailed mechanism, but at later times (0.1 and 1.0 s), the two models are in good agreement (see Figure 1). This disagreement in $\text{H}\cdot$ atom concentration at early times is due to the breakdown of the assumption that all of the ion-molecule reactions are fast. This is not strictly true for the neutralization of H_3O^+ by CO_2^- (Reaction 28), which is somewhat slower than the other ion-molecule reactions because of the low concentrations of the reactants.

The simplified reaction model (Table 4) requires much less computation time than the full reaction set (Reactions 1 to 38). The two sets were integrated numerically to 1-s chemical time using the MAKSIM computer code [36-38] running on a VAX 8650 computer under the VAX/VMS operating system. The simplified reaction set required 1.12 s of computation time and the full reaction set required 5.22 s. The simplified radical production model in Table 4 should be sufficient to determine radical yields during irradiation of the moist flue gases generated by combustion of organic materials in air. Small adjustments in the relative rates of the primary radiolysis reactions are required to correct for differences in stopping power of the components of the mixture if a different initial gas composition is used.

If we make the additional approximation that



is much faster than



then the radical yields may be written as linear algebraic functions of the concentrations of the major flue gas components:

$$\begin{aligned} G(\text{H}\cdot) &= (41.5[\text{N}_2] + 52.8[\text{O}_2] + 73.9[\text{H}_2\text{O}] + 65.2[\text{CO}_2]) / \langle n_e \rangle \\ G(\cdot\text{OH}) &= (41.5[\text{N}_2] + 52.8[\text{O}_2] + 62.5[\text{H}_2\text{O}] + 65.2[\text{CO}_2]) / \langle n_e \rangle \\ G(\text{N}\cdot) &= 52.3[\text{N}_2] / \langle n_e \rangle \\ G(\text{O}\cdot) &= (5.4[\text{N}_2] + 22.5[\text{O}_2] + 10.2[\text{H}_2\text{O}] + 11.2[\text{CO}_2]) / \langle n_e \rangle \\ G(\text{CO}) &= (19.6[\text{O}_2] + 20.5[\text{CO}_2]) / \langle n_e \rangle \end{aligned}$$

where $\langle n_e \rangle$ is the average number of electrons per molecule in the flue gas mixture, the concentrations are in mole fractions and the G-values are in molecule $\cdot(100 \text{ eV})^{-1}$. The above equations include correction factors for the difference in stopping power of the components of the flue gas mixture. In a typical combustion flue gas, the concentration of CO_2 is greater than, or equal to, the water vapour concentration. Therefore, the approximation that Reaction 20 can be neglected compared with Reaction 38 introduces an error of <16% into the calculated $\text{O}\cdot$ atom yield. The radical yields calculated for a flue gas containing 68% N_2 , 15.5% O_2 , 10.5% H_2O and 6% CO_2 using the above equations are $G(\text{H}\cdot) = 3.35$, $G(\cdot\text{OH}) = 3.26$, $G(\text{N}\cdot) = 2.47$, $G(\text{O}\cdot) = 0.62$, and $G(\text{CO}) = 0.30$ molecule $\cdot(100 \text{ eV})^{-1}$. These are to be compared with the yields calculated using the full radical production mechanism, $G(\text{H}\cdot) = 3.34$, $G(\cdot\text{OH}) = 3.26$, $G(\text{N}\cdot) = 2.47$, $G(\text{O}\cdot) = 0.68$, and

$G(\text{CO}) = 0.24 \text{ molecule} \cdot (100 \text{ eV})^{-1}$. The yields of $\text{H} \cdot$ atom, $\cdot\text{OH}$ radical, and $\text{N} \cdot$ atom calculated from the above equations are in good quantitative agreement with those calculated from the full reaction mechanism, but the approximate $\text{O} \cdot$ atom yield is low by about $0.06 \text{ molecule} \cdot (100 \text{ eV})^{-1}$ (9%) and the CO yield is high by about $0.06 \text{ molecule} \cdot (100 \text{ eV})^{-1}$ (25%) because of the inadequacy of the assumption that Reaction 20 can be neglected with respect to Reaction 38. In a more typical flue gas mixture, the errors in the yields of $\text{O} \cdot$ and CO would be smaller because the ratio of $[\text{CO}_2]/[\text{H}_2\text{O}]$ is larger than in the gas mixture used here. The above equations for radical yields in combustion flue gases should give good agreement with more detailed calculations for gas mixtures containing at least 1 vol.% of each of water vapour, carbon dioxide and oxygen, and in which the carbon dioxide concentration is greater than, or equal to, the water vapour concentration.

The normalized sensitivity coefficients for the dependence of the NO , NO_2 and HNO_3 concentrations on the rates of Reactions 1 to 66 at a time of 1 s (10-kGy dose) were calculated. An analysis of these coefficients shows a similar pattern of dependence of NO_x species concentrations on the rates of Reactions 1 to 38 to that noted above for the radical production mechanism, i.e., large normalized sensitivity coefficients for the initial species production reactions and relatively small corresponding values for most of the ion-molecule reactions. The normalized sensitivity coefficients for the dependence of NO , NO_2 and HNO_3 concentrations on the rates of Reactions 39 to 66 at 1 s and 10-kGy dose are shown in Table 5. The normalized sensitivity coefficients for the dependence of the NO_x concentrations on the rates of Reactions 39-42, 44, 46, 47, 54 and 64 are all less than 10^{-3} , indicating that these reactions could potentially be removed from the mechanism without affecting the NO_x concentrations at 1 s significantly. Reactions 39, 41, 42, 44 and 46 are radical-radical reactions and are relatively unimportant at a dose rate of $10 \text{ kGy} \cdot \text{s}^{-1}$, but would be more important at higher dose rates (or higher doses, see below). Reaction 40 ($\text{H} \cdot + \text{O}_2 \rightarrow \text{HO}_2$) has a small normalized sensitivity coefficient because it is relatively fast and there are no other $\text{H} \cdot$ atom reactions in the model. Nevertheless, it is an important channel leading to NO_x oxidation by HO_2 and, thus, it cannot be removed from the mechanism except by replacing $\text{H} \cdot$ products with HO_2 in the reactions in Table 4. The reaction of CO with $\cdot\text{OH}$ (and O_2) (Reaction 47) has relatively little effect on the NO_x species concentrations at low doses because CO is present at low concentration, and both $\cdot\text{OH}$ and HO_2 react with NO . Reactions 54 and 64 are much slower than other reactions of O_3 (Reaction 53) and N_2O_5 (Reaction 65) and could potentially be removed without affecting the concentrations of NO_x species.

The sensitivity analysis at 1 s (10 kGy dose) indicates that a simplified NO_x reaction mechanism consisting of the radical production reactions from Table 4 and the NO_x species reactions from Table 1 (Reactions 39 to 66), excluding Reactions 39, 41, 42, 44, 46, 47, 54 and 64, could be used. This simplified NO_x reaction model reproduces accurately the NO and HNO_3 concentrations given by the full mechanism at times up to 5 s (50 kGy), as shown in Figure 2. The NO_2 concentration at 1 s given by the simplified model is accurate, but the NO_2 concentration at 5 s is about 15% lower than that given by the full mechanism (Figure 2). The sensitivity data for the NO_2 concentration at 5 s indicates that the rates of Reactions 42, 46, 47, 54 and 64 have a larger influence on the $[\text{NO}_2]$ at 5 s than they do at 1 s.

This is mainly due to the increased importance of radical-radical reactions at doses sufficient to give nearly quantitative conversion of NO and NO₂ to HNO₃ and HNO₂. The 15% error in the NO₂ concentration predicted by the simplified model at 5 s indicates that caution must be used when sensitivity data at a single time is used to aid in model reduction. In general, a simplified model has a more limited range of applicability than the full mechanism it was obtained from. The simplified NO_x reaction model described above gives good agreement with the full mechanism up to about 90% NO_x removal.

A sensitivity analysis of the NO_x/SO₂ reaction set was also performed. The normalized sensitivity coefficients for the dependence of NO, NO₂ and SO₂ concentrations on the reaction rates at a time of 1 s and the corresponding sensitivities for HNO₃, H₂SO₄ and HSO₅N at 3 s were calculated. These sensitivities indicate that similar simplifications to those made above for the NO_x reaction mechanism are possible for those reactions that also appear in the NO_x/SO₂ reaction model. The sensitivity data for NO, NO₂ and SO₂ concentrations at 1 s (10-kGy dose) are presented in Table 6. The normalized sensitivity coefficients at 1 s for NO, NO₂ and SO₂ are all less than 10⁻³ for Reactions 63-66, 68, 70-77 and 81-83. The sensitivities of Reactions 63 to 66 are relatively low because there are no significant back reactions of NO₃, but these reactions should still be retained in a reduced model. Reaction 68 (SO₂ + HO₂ → SO₃ + ·OH) is much slower than the reactions of the HO₂ radical with NO and NO₂, but this reaction would become more significant as the NO_x species concentrations decline at higher doses. Reaction 70 (SO₃ + H₂O → H₂SO₄) is the only significant reaction channel for SO₃; Reaction 83 (SO₃ + O· → SO₂ + O₂) can be neglected. Reactions 73 (HSO₃ + NO₂ → HSO₅N) and 75 (HSO₃ + O₂ → HSO₅) are the significant reactions of the HSO₃ radical and, thus, the radical-radical reactions of HSO₃ (Reactions 71, 72, 74, 76 and 77) can be neglected. Reaction 81 (HSO₄ + NO → HSO₅N) is the only reaction channel for HSO₄ radical consumption and it must be retained. Reaction 82 (HSO₅ + N· → HSO₄ + NO) is much slower than the reactions of HSO₅ with NO (Reactions 78 and 79) and SO₂ (Reaction 80), and it may be neglected.

The radical production reactions in Table 4 and the NO_x/SO₂ reactions in Table 7 together form a simplified reaction model for the radiolytic oxidation of NO_x and SO₂ in a flue gas. The dependence of the major reactant and product species on radiation dose predicted by the two models are compared in Figure 3. Reactions of NO_x and SO₂ species have been retained or removed, as discussed in the previous paragraph. It was also necessary to include the reactions of the HO₂ radical with itself (Reaction 42) and with the ·OH radical (Reaction 46) in order to reproduce the NO, NO₂, HNO₃, SO₂, H₂SO₄ and HSO₅N concentration profiles given by the full model within ±1% over the dose range from 0 to 120 kGy (98% SO₂ removal and 80% NO_x removal). Removing these two reactions (42 and 46) from the model caused the SO₂ concentration to fall more rapidly than predicted by the full mechanism at doses above 60 kGy. The simplified NO_x/SO₂ reaction model required about 50% less computation time to integrate to 12-s chemical time (120-kGy dose) than the full reaction mechanism. The simplified model for the radiation treatment of combustion gases containing NO_x and SO₂ presented in Tables 4 and 7 appears to be adequate to reproduce the major species concentration profiles given by the full reaction mechanism.

5. CONCLUSIONS

Sensitivity analysis techniques and chemical knowledge have been used to formulate simplified models for radical production, NO_x and NO_x/SO_2 reaction mechanisms for the radiation treatment of combustion flue gases. The sensitivity analysis results are a useful guide for identifying reactions that could potentially be removed from the full reaction mechanism, but some chemical knowledge is required to obtain simplified models that give major species profiles that are in good agreement with the predictions of the full mechanism. This is especially true if sensitivity information is not available for all chemical times of interest.

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TABLE 1

REACTION MECHANISM FOR RADIOLYTIC OXIDATION OF NITROGEN OXIDES
WITH RATE CONSTANTS FOR 25°C IN dm³·mol⁻¹·s⁻¹ UNITS [17]

Chemical Reaction					Rate Constant	
1.	N ₂		→ N ₂ ⁺	+ e ⁻	6.54 x 10 ⁻⁵	
2.	N ₂		→ N ⁺	+ N·	+ e ⁻	1.99 x 10 ⁻⁵
3.	N ₂		→ N·	+ N·		3.39 x 10 ⁻⁵
4.	N ₂		→ N ₂ ⁺			8.35 x 10 ⁻⁶
5.	O ₂		→ O ₂ ⁺	+ e ⁻		6.82 x 10 ⁻⁵
6.	O ₂		→ O ⁺	+ O·	+ e ⁻	4.04 x 10 ⁻⁵
7.	O ₂		→ O·	+ O·		2.96 x 10 ⁻⁶
8.	H ₂ O		→ H ₂ O ⁺	+ e ⁻		4.10 x 10 ⁻⁵
9.	H ₂ O		→ OH ⁺	+ H·	+ e ⁻	1.17 x 10 ⁻⁵
10.	H ₂ O		→ H ⁺	+ ·OH	+ e ⁻	1.38 x 10 ⁻⁵
11.	H ₂ O		→ H·	+ ·OH		7.37 x 10 ⁻⁵
12.	H ₂ O		→ H ₂	+ O·		9.27 x 10 ⁻⁶
13.	CO ₂		→ CO ₂ ⁺	+ e ⁻		1.01 x 10 ⁻⁴
14.	CO ₂		→ CO ⁺	+ O·	+ e ⁻	2.31 x 10 ⁻⁵
15.	CO ₂		→ O ⁺	+ CO	+ e ⁻	9.51 x 10 ⁻⁶
16.	OH ⁺	+ H ₂ O	→ H ₃ O ⁺	+ O·		9.0 x 10 ¹¹
17.	N ₂ ⁺	+ H ₂ O	→ H ₂ O ⁺	+ N ₂		1.4 x 10 ¹²
18.	N ⁺	+ H ₂ O	→ H ₂ O ⁺	+ N·		1.4 x 10 ¹²
19.	O ₂ ⁺	+ H ₂ O	→ H ₂ O ⁺	+ O ₂		1.0 x 10 ¹⁰
20.	O ⁺	+ H ₂ O	→ H ₂ O ⁺	+ O·		1.4 x 10 ¹¹
21.	H ₂ O ⁺	+ H ₂ O	→ H ₃ O ⁺	+ ·OH		7.2 x 10 ¹¹
22.	N ₂ ⁺	+ O ₂	→ N ₂	+ O ₂ ⁺		2.5 x 10 ¹⁰
23.	e ⁻	+ O ₂	→ O ₂ ⁻			3.2 x 10 ¹⁰
24.	H ₃ O ⁺	+ O ₂ ⁻	→ H·	+ O ₂	+ H ₂ O	2.5 x 10 ¹¹
25.	H ₃ O ⁺	+ e ⁻	→ H·	+ H ₂ O		2.5 x 10 ¹¹

continued...

TABLE 1 (continued)

Chemical Reaction					Rate Constant
26.	e^-	+ CO_2	$\rightarrow CO_2^-$		8.5×10^4
27.	O_2^-	+ CO_2	$\rightarrow CO_2^-$	+ O_2	2.5×10^{11}
28.	CO_2^-	+ H_3O^+	$\rightarrow H\cdot$	+ H_2O + CO_2	1.0×10^{12}
29.	O_2^+	+ CO_2^-	$\rightarrow CO$	+ O_2 + $O\cdot$	2.5×10^{11}
30.	O_2^-	+ OH^+	$\rightarrow O_2$	+ $\cdot OH$	2.0×10^{11}
31.	CO_2^-	+ OH^+	$\rightarrow CO_2$	+ $\cdot OH$	2.0×10^{11}
32.	N_2^+	+ O_2	$\rightarrow N_2$	+ $O\cdot$ + $O\cdot$	1.2×10^9
33.	N_2^+	+ O_2	$\rightarrow N_2$	+ O_2	6.0×10^8
34.	H^+	+ H_2O	$\rightarrow H_3O^+$		1.0×10^{10}
35.	CO^+	+ H_2O	$\rightarrow H_2O^+$	+ CO	1.0×10^{12}
36.	CO_2^+	+ H_2O	$\rightarrow H_2O^+$	+ CO_2	1.0×10^{12}
37.	CO_2^+	+ O_2	$\rightarrow O_2^+$	+ CO_2	6.0×10^{10}
38.	O^+	+ CO_2	$\rightarrow CO$	+ O_2^+	7.2×10^{11}
39.	$N\cdot$	+ $N\cdot$	$\rightarrow N_2$		1.0×10^8
40.	$H\cdot$	+ O_2	$\rightarrow HO_2$		6.5×10^9
41.	$\cdot OH$	+ $\cdot OH$	$\rightarrow H_2O_2$		1.8×10^9
42.	HO_2	+ HO_2	$\rightarrow H_2O_2$	+ O_2	2.2×10^9
43.	$O\cdot$	+ O_2	$\rightarrow O_3$		8.2×10^6
44.	$\cdot OH$	+ $\cdot OH$	$\rightarrow H_2O$	+ $O\cdot$	1.4×10^9
45.	$N\cdot$	+ O_2	$\rightarrow NO$	+ $O\cdot$	1.5×10^9
46.	$\cdot OH$	+ HO_2	$\rightarrow H_2O$	+ O_2	5.6×10^{10}
47.	CO	+ $\cdot OH (+O_2)^*$	$\rightarrow CO_2$	+ HO_2	8.2×10^7
48.	NO	+ $\cdot OH$	$\rightarrow HNO_2$		4.9×10^9
49.	NO_2	+ $\cdot OH$	$\rightarrow HNO_3$		4.8×10^9
50.	NO	+ $O\cdot$	$\rightarrow NO_2$		1.6×10^9
51.	NO_2	+ $O\cdot$	$\rightarrow NO_3$		1.3×10^9
52.	NO_2	+ $O\cdot$	$\rightarrow NO$	+ O_2	5.6×10^9
53.	NO	+ O_3	$\rightarrow NO_2$	+ O_2	1.2×10^7
54.	NO_2	+ O_3	$\rightarrow NO_3$	+ O_2	4.8×10^4

continued...

TABLE 1 (concluded)

Chemical Reaction					Rate Constant
55.	NO	+ HO ₂	→ NO ₂	+ ·OH	6.0 × 10 ⁹
56.	NO ₂	+ HO ₂	→ HNO ₂	+ O ₂	1.8 × 10 ⁸
57.	NO	+ N·	→ N ₂	+ O·	1.3 × 10 ¹⁰
58.	NO ₂	+ N·	→ NO	+ NO	3.5 × 10 ⁹
59.	NO ₂	+ N·	→ N ₂ O	+ O·	4.6 × 10 ⁹
60.	HNO ₂	+ ·OH	→ NO ₂	+ H ₂ O	4.1 × 10 ⁹
61.	HNO ₂	+ HNO ₂	→ NO	+ NO ₂ + H ₂ O	1.8 × 10 ⁶
62.	HNO ₂	+ HNO ₃	→ NO ₂	+ NO ₂ + H ₂ O	8.2 × 10 ⁴
63.	NO ₂	+ NO ₃	→ N ₂ O ₅		1.8 × 10 ⁹
64.	N ₂ O ₅		→ NO ₂	+ NO ₃	2.9 × 10 ⁻¹
65.	N ₂ O ₅	+ H ₂ O	→ HNO ₃	+ HNO ₃	2.5 × 10 ³
66.	NO	+ NO ₃	→ NO ₂	+ NO ₂	6.0 × 10 ⁹

* Species that is consumed in the reaction, but whose concentration does not appear in the rate equation.

TABLE 2

RATE CONSTANTS FOR NO_x REACTIONS WITH SIGNFICIANT TEMPERATURE DEPENDENCES
AND FOR REACTIONS OF SULPHUR-CONTAINING SPECIES AT 120°C FOR THE RADIATION
TREATMENT OF COMBUSTION FLUE GASES (dm³·mol⁻¹·s⁻¹ UNITS) [19]

Chemical Reaction				Rate Constant
43.	O·	+ O ₂	→ O ₃	6.6 × 10 ⁶
48.	NO	+ ·OH	→ HNO ₂	4.8 × 10 ⁹
50.	NO	+ O·	→ NO ₂	7.8 × 10 ⁸
52.	NO ₂	+ O·	→ NO + O ₂	4.9 × 10 ⁹
53.	NO	+ O ₃	→ NO ₂ + O ₂	2.1 × 10 ⁷
60.	HNO ₂	+ ·OH	→ NO ₂ + H ₂ O	1.5 × 10 ⁸
61.	HNO ₂	+ HNO ₂	→ NO + NO ₂ + H ₂ O	1.5 × 10 ⁶
64.	N ₂ O ₅		→ NO ₂ + NO ₃	1.5 × 10 ⁴
67.	SO ₂	+ ·OH	→ HSO ₃	3.5 × 10 ⁸
68.	SO ₂	+ HO ₂	→ SO ₃ + ·OH	9.0 × 10 ⁵
69.	SO ₂	+ O·	→ SO ₃	4.0 × 10 ⁷
70.	SO ₃	+ H ₂ O	→ H ₂ SO ₄	5.5 × 10 ⁸
71.	HSO ₃	+ ·OH	→ H ₂ SO ₄	5.0 × 10 ⁹
72.	HSO ₃	+ ·OH	→ SO ₃ + H ₂ O	5.0 × 10 ⁹
73.	HSO ₃	+ NO ₂	→ HSO ₅ N	5.0 × 10 ⁸
74.	HSO ₃	+ HO ₂	→ H ₂ SO ₅	5.0 × 10 ⁹
75.	HSO ₃	+ O ₂	→ HSO ₅	4.0 × 10 ⁸
76.	HSO ₃	+ HSO ₃	→ H ₂ S ₂ O ₆	3.0 × 10 ⁸
77.	HSO ₅	+ HSO ₃	→ HSO ₄ + HSO ₄	5.0 × 10 ⁷
78.	HSO ₅	+ NO	→ HSO ₄ + NO ₂	5.0 × 10 ⁹
79.	HSO ₅	+ NO	→ HSO ₆ N	5.0 × 10 ⁹
80.	HSO ₅	+ SO ₂	→ HSO ₄ + SO ₃	1.0 × 10 ⁹
81.	HSO ₄	+ NO	→ HSO ₅ N	1.0 × 10 ⁹
82.	HSO ₅	+ N·	→ HSO ₄ + NO	3.5 × 10 ⁹
83.	SO ₃	+ O·	→ SO ₂ + O ₂	4.2 × 10 ⁸

TABLE 3

NORMALIZED SENSITIVITY COEFFICIENTS, $d(\ln[i])/d(\ln k_j)$, FOR THE DEPENDENCE OF RADICAL CONCENTRATIONS ON THE RATE CONSTANTS IN THE RADICAL PRODUCTION MECHANISM (REACTIONS 1 TO 38 IN TABLE 1) AT 1-s TIME AND 10-kGy DOSE

Normalized Sensitivity Coefficients					
Reaction	H·	·OH	N·	O·	CO
1	4.5×10^{-1}	4.6×10^{-1}	-2.4×10^{-14}	-3.4×10^{-5}	4.7×10^{-5}
2	1.4×10^{-1}	1.4×10^{-1}	3.7×10^{-1}	-1.4×10^{-5}	1.4×10^{-5}
3	-1.0×10^{-5}	-1.0×10^{-5}	6.3×10^{-1}	-6.4×10^{-6}	-6.6×10^{-10}
4	-2.1×10^{-6}	-2.1×10^{-6}	-7.3×10^{-13}	3.8×10^{-1}	-1.5×10^{-8}
5	1.1×10^{-1}	1.1×10^{-1}	-3.1×10^{-15}	-2.3×10^{-6}	2.8×10^{-5}
6	6.3×10^{-2}	6.5×10^{-2}	-1.8×10^{-15}	3.9×10^{-1}	6.6×10^{-1}
7	-2.5×10^{-7}	-2.6×10^{-7}	-1.1×10^{-18}	4.6×10^{-2}	-9.8×10^{-7}
8	4.4×10^{-2}	4.5×10^{-2}	-1.3×10^{-15}	-3.3×10^{-6}	4.4×10^{-6}
9	2.5×10^{-2}	-8.3×10^{-7}	-3.6×10^{-16}	6.1×10^{-2}	1.3×10^{-6}
10	1.5×10^{-2}	1.5×10^{-2}	-4.3×10^{-16}	-1.1×10^{-6}	1.5×10^{-6}
11	7.8×10^{-2}	8.0×10^{-2}	-2.3×10^{-15}	-6.4×10^{-6}	6.8×10^{-6}
12	-7.5×10^{-7}	-6.5×10^{-7}	-2.9×10^{-16}	4.8×10^{-2}	8.5×10^{-7}
13	6.1×10^{-2}	6.3×10^{-2}	-1.8×10^{-15}	-4.4×10^{-6}	7.0×10^{-6}
14	1.4×10^{-2}	1.4×10^{-2}	-4.1×10^{-16}	6.9×10^{-2}	2.0×10^{-1}
15	5.8×10^{-3}	5.9×10^{-3}	-1.7×10^{-16}	7.2×10^{-3}	1.4×10^{-1}
16*	1.2×10^{-9}	-1.3×10^{-9}	-3.1×10^{-26}	6.1×10^{-9}	-7.3×10^{-14}
17*	1.3×10^{-7}	1.3×10^{-7}	1.0×10^{-14}	-6.2×10^{-7}	1.8×10^{-6}
18*	1.2×10^{-11}	2.4×10^{-11}	3.1×10^{-11}	-2.4×10^{-13}	-6.4×10^{-13}
19*	2.0×10^{-6}	2.0×10^{-6}	-5.2×10^{-20}	-9.6×10^{-6}	-2.7×10^{-5}

continued...

TABLE 3 (concluded)

Reaction	H·	·OH	N·	O·	CO
20	3.1×10^{-7}	3.2×10^{-7}	3.1×10^{-18}	6.4×10^{-2}	-1.8×10^{-1}
21*	1.4×10^{-10}	2.9×10^{-10}	3.6×10^{-20}	-2.9×10^{-12}	-8.1×10^{-12}
22*	-1.3×10^{-7}	-1.3×10^{-7}	2.7×10^{-16}	6.2×10^{-7}	1.8×10^{-6}
23*	1.8×10^{-9}	-1.3×10^{-11}	5.3×10^{-23}	6.2×10^{-11}	1.7×10^{-10}
24*	1.9×10^{-10}	8.3×10^{-13}	5.4×10^{-24}	-3.7×10^{-12}	-1.1×10^{-11}
25*	6.1×10^{-10}	2.7×10^{-12}	1.8×10^{-23}	-1.2×10^{-11}	-3.5×10^{-11}
26*	2.4×10^{-15}	-1.7×10^{-17}	7.2×10^{-29}	8.3×10^{-17}	2.3×10^{-16}
27*	5.5×10^{-10}	-3.8×10^{-12}	1.7×10^{-23}	1.9×10^{-11}	5.3×10^{-11}
28*	2.4×10^{-4}	1.1×10^{-6}	6.9×10^{-18}	-4.8×10^{-6}	-1.4×10^{-5}
29*	-2.0×10^{-6}	-2.0×10^{-6}	5.7×10^{-20}	9.6×10^{-6}	2.7×10^{-5}
30*	-3.9×10^{-15}	4.0×10^{-15}	2.9×10^{-32}	-1.9×10^{-14}	-5.8×10^{-20}
31*	-1.2×10^{-9}	1.3×10^{-9}	9.3×10^{-27}	-6.1×10^{-9}	-1.8×10^{-14}
32	-6.9×10^{-7}	-7.1×10^{-7}	4.9×10^{-13}	1.3×10^{-1}	-2.7×10^{-6}
33	6.9×10^{-7}	7.1×10^{-7}	2.4×10^{-13}	-1.3×10^{-1}	2.7×10^{-6}
34*	1.7×10^{-10}	7.2×10^{-13}	-5.0×10^{-24}	-3.5×10^{-12}	-9.7×10^{-12}
35*	1.6×10^{-12}	3.4×10^{-12}	1.8×10^{-22}	-3.4×10^{-14}	4.6×10^{-11}
36*	5.1×10^{-8}	5.3×10^{-8}	-1.7×10^{-21}	-2.5×10^{-7}	-7.2×10^{-7}
37*	-5.1×10^{-8}	-5.3×10^{-8}	1.4×10^{-21}	2.5×10^{-7}	7.2×10^{-7}
38	-3.1×10^{-7}	-3.2×10^{-7}	3.1×10^{-18}	-6.4×10^{-2}	1.8×10^{-1}

* Reactions that are candidates for elimination in the selection of a simplified model because of their small normalized sensitivity coefficients.

TABLE 4

SIMPLIFIED MODEL FOR RADICAL PRODUCTION IN THE RADIOLYSIS OF A COMBUSTION
FLUE GAS AT A DOSE RATE OF 10 kGy·s⁻¹ (dm³·mol⁻¹·s⁻¹ UNITS)

Chemical Reaction					Rate Constant
N ₂	(+ H ₂ O)	→ ·OH	+ H·	+ N ₂	8.53 × 10 ⁻⁵ = k ₁ + k ₂
N ₂		→ N·	+ N·		5.38 × 10 ⁻⁵ = k ₂ + k ₃
N ₂	(+ O ₂)	→ O·	+ O·	+ N ₂	5.57 × 10 ⁻⁶ = 0.667k ₄
O ₂	(+ H ₂ O)	→ ·OH	+ H·	+ O ₂	6.82 × 10 ⁻⁵ = k ₅
O ₂		→ O ⁺	+ O·	+ e ⁻	4.04 × 10 ⁻⁵ = k ₆
O ⁺ + H ₂ O	(+ e ⁻)	→ ·OH	+ H·	+ O·	1.4 × 10 ¹¹ = k ₂₀
O ⁺	+ CO ₂	→ CO	+ O ₂ ⁺		7.2 × 10 ¹¹ = k ₃₈
O ₂ ⁺ + H ₂ O	(+ e ⁻)	→ ·OH	+ H·	+ O ₂	1.0 × 10 ¹⁰ = k ₁₉
O ₂		→ O·	+ O·		2.96 × 10 ⁻⁶ = k ₇
H ₂ O		→ ·OH	+ H·		1.285 × 10 ⁻⁴ = k ₈ + k ₁₀ + k ₁₁
H ₂ O		→ H·	+ H·	+ O·	1.17 × 10 ⁻⁵ = k ₉
H ₂ O		→ H ₂	+ O·		9.27 × 10 ⁻⁶ = k ₁₂
CO ₂	(+ H ₂ O)	→ ·OH	+ H·	+ CO ₂	1.24 × 10 ⁻⁴ = k ₁₃ + k ₁₄
CO ₂		→ CO	+ O·		2.31 × 10 ⁻⁵ = k ₁₄
CO ₂		→ O ⁺	+ CO	+ e ⁻	9.51 × 10 ⁻⁶ = k ₁₅

Note:

1. Species in parentheses are consumed in the reaction but their concentrations do not appear in the rate equation.
2. Reaction rate constants were derived from the rate constants of the radical production mechanism, Reactions 1 to 38 in Table 1, as indicated.

TABLE 5

NORMALIZED SENSITIVITY COEFFICIENTS, $d(\ln[i])/d(\ln k_j)$, FOR THE DEPENDENCE OF NO, NO₂ AND HNO₃ CONCENTRATIONS ($[i]$) ON THE RATE CONSTANTS (k_j) OF REACTIONS 39 TO 66 IN THE NO_x REACTION MECHANISM (TABLE 1) AT 1-s TIME AND 10-kGy DOSE

Normalized Sensitivity Coefficients			
Reaction	NO	NO ₂	HNO ₃
39*	-2.5×10^{-12}	-1.2×10^{-12}	-3.3×10^{-13}
40*	-1.9×10^{-8}	3.8×10^{-9}	2.3×10^{-8}
41*	5.6×10^{-6}	1.1×10^{-6}	-1.1×10^{-5}
42*	1.3×10^{-5}	-3.7×10^{-6}	-1.2×10^{-5}
43	-1.8×10^{-1}	9.8×10^{-2}	7.3×10^{-2}
44*	1.9×10^{-6}	1.9×10^{-6}	-6.5×10^{-6}
45	1.1×10^{-2}	3.2×10^{-3}	-2.2×10^{-3}
46*	2.8×10^{-4}	-3.9×10^{-5}	-3.3×10^{-4}
47*	-3.0×10^{-4}	1.7×10^{-4}	1.1×10^{-4}
48	-1.1×10^{-1}	2.1×10^{-1}	-4.2×10^{-1}
49	1.0×10^{-1}	-2.5×10^{-1}	4.6×10^{-1}
50	-3.2×10^{-2}	1.7×10^{-2}	1.7×10^{-2}
51	-1.6×10^{-2}	-1.7×10^{-3}	2.5×10^{-2}
52	2.2×10^{-1}	-1.1×10^{-1}	-1.1×10^{-1}
53	-5.7×10^{-3}	2.4×10^{-3}	4.3×10^{-3}
54*	1.2×10^{-4}	-4.2×10^{-4}	5.5×10^{-4}

continued...

TABLE 5 (concluded)

Normalized Sensitivity Coefficients			
Reaction	NO	NO ₂	HNO ₃
55	-2.5×10^{-2}	1.1×10^{-2}	2.2×10^{-2}
56	2.5×10^{-2}	-1.1×10^{-2}	-2.2×10^{-2}
57	-1.1×10^{-2}	-1.8×10^{-3}	2.7×10^{-3}
58	1.1×10^{-3}	-5.4×10^{-4}	-5.2×10^{-4}
59	-1.4×10^{-3}	-8.1×10^{-4}	-7.2×10^{-6}
60	5.2×10^{-3}	3.3×10^{-2}	-4.8×10^{-2}
61	6.3×10^{-2}	5.0×10^{-3}	3.7×10^{-2}
62	-2.4×10^{-3}	1.6×10^{-2}	-2.4×10^{-2}
63	3.9×10^{-3}	-1.1×10^{-2}	1.5×10^{-2}
64*	-8.6×10^{-5}	2.4×10^{-4}	-3.1×10^{-4}
65	6.0×10^{-5}	-1.2×10^{-4}	5.2×10^{-3}
66	-3.9×10^{-3}	1.1×10^{-2}	-1.5×10^{-2}

Note:

1. The sensitivities of the NO_x concentrations to the rate constants of Reactions 1 to 38 are similar to those of the radical production mechanism (Table 3).
2. Reactions indicated with an asterisk (*) are candidates for elimination in the selection of a simplified model because of their small normalized sensitivity coefficients.

TABLE 6

NORMALIZED SENSITIVITY COEFFICIENTS, $d(\ln[i])/d(\ln k_j)$, FOR THE DEPENDENCE OF NO, NO₂ AND SO₂ CONCENTRATIONS ([i]) ON THE RATE CONSTANTS (k_j) OF REACTIONS 63 to 83 IN THE NO_x/SO₂ REACTION MECHANISM (TABLES 1 AND 2) AT 1-s TIME AND 10-kGy DOSE

Normalized Sensitivity Coefficients			
Reaction	NO	NO ₂	SO ₂
63*	7.8 x 10 ⁻⁶	-2.3 x 10 ⁻⁵	-1.9 x 10 ⁻⁷
64*	-7.8 x 10 ⁻⁶	2.3 x 10 ⁻⁵	1.9 x 10 ⁻⁷
65*	6.7 x 10 ⁻⁶	-1.9 x 10 ⁻⁵	-1.4 x 10 ⁻⁷
66*	-9.6 x 10 ⁻⁶	2.6 x 10 ⁻⁵	2.2 x 10 ⁻⁷
67	-8.6 x 10 ⁻²	9.9 x 10 ⁻³	-5.8 x 10 ⁻²
68*	1.4 x 10 ⁻⁴	-6.9 x 10 ⁻⁵	-9.8 x 10 ⁻⁵
69	1.5 x 10 ⁻³	-6.1 x 10 ⁻⁴	-2.2 x 10 ⁻³
70*	-4.2 x 10 ⁻¹¹	1.9 x 10 ⁻¹¹	-7.4 x 10 ⁻¹¹
71*	4.6 x 10 ⁻⁸	1.8 x 10 ⁻⁹	3.1 x 10 ⁻⁹
72*	4.6 x 10 ⁻⁸	1.8 x 10 ⁻⁹	3.1 x 10 ⁻⁹
73*	8.1 x 10 ⁻⁵	-4.3 x 10 ⁻⁵	4.9 x 10 ⁻⁶
74*	4.7 x 10 ⁻⁸	-6.2 x 10 ⁻⁹	2.3 x 10 ⁻⁹
75*	-8.1 x 10 ⁻⁵	4.3 x 10 ⁻⁵	-4.9 x 10 ⁻⁶
76*	4.4 x 10 ⁻¹²	-6.6 x 10 ⁻¹⁴	2.6 x 10 ⁻¹³
77*	7.1 x 10 ⁻¹²	-3.6 x 10 ⁻¹²	1.4 x 10 ⁻¹²
78	-1.8 x 10 ⁻²	8.6 x 10 ⁻³	2.6 x 10 ⁻³
79	1.4 x 10 ⁻²	-6.7 x 10 ⁻³	2.7 x 10 ⁻³

continued...

TABLE 6 (concluded)

Normalized Sensitivity Coefficients

Reaction	NO	NO ₂	SO ₂
80	3.9 x 10 ⁻³	-1.9 x 10 ⁻³	-5.2 x 10 ⁻³
81*	-1.3 x 10 ⁻⁵	-1.9 x 10 ⁻⁶	-2.4 x 10 ⁻⁷
82*	9.8 x 10 ⁻¹⁰	-4.6 x 10 ⁻¹⁰	1.0 x 10 ⁻¹⁰
83*	4.3 x 10 ⁻¹¹	-1.9 x 10 ⁻¹¹	7.4 x 10 ⁻¹¹

Note:

1. The sensitivities of the NO, NO₂ and SO₂ concentrations to the rate constants of Reactions 1 to 62 are similar to those of the NO_x reaction mechanism (Tables 3 and 5).
2. Reactions indicated with an asterisk (*) are candidates for elimination in the selection of a simplified model because of their small normalized sensitivity coefficients.

TABLE 7

SIMPLIFIED MECHANISM FOR THE REACTIONS OF NO_x AND SO₂
IN THE RADIATION TREATMENT OF FLUE GASES

Chemical Reaction	Rate Constant (at 120°C) (dm ³ ·mol ⁻¹ ·s ⁻¹)
40. H· + O ₂ → HO ₂	6.5 × 10 ⁹
42. HO ₂ + HO ₂ → H ₂ O ₂ + O ₂	2.2 × 10 ⁹
43. O· + O ₂ → O ₃	6.6 × 10 ⁶
45. N· + O ₂ → NO + O·	1.5 × 10 ⁹
46. ·OH + HO ₂ → H ₂ O + O ₂	5.6 × 10 ¹⁰
47. CO + ·OH (+O ₂) → CO ₂ + HO ₂	8.2 × 10 ⁷
48. NO + ·OH → HNO ₂	4.8 × 10 ⁹
49. NO ₂ + ·OH → HNO ₃	4.8 × 10 ⁹
50. NO + O· → NO ₂	7.8 × 10 ⁸
51. NO ₂ + O· → NO ₃	1.3 × 10 ⁹
52. NO ₂ + O· → NO + O ₂	4.9 × 10 ⁹
53. NO + O ₃ → NO ₂ + O ₂	2.1 × 10 ⁷
54. NO ₂ + O ₃ → NO ₃ + O ₂	4.8 × 10 ⁴
55. NO + HO ₂ → NO ₂ + ·OH	6.0 × 10 ⁹
56. NO ₂ + HO ₂ → HNO ₂ + O ₂	1.8 × 10 ⁸
57. NO + N· → N ₂ + O·	1.3 × 10 ¹⁰
58. NO ₂ + N· → NO + NO	3.5 × 10 ⁹
59. NO ₂ + N· → N ₂ O + O·	4.6 × 10 ⁹
60. HNO ₂ + ·OH → NO ₂ + H ₂ O	1.5 × 10 ⁸
61. HNO ₂ + HNO ₂ → NO + NO ₂ + H ₂ O	1.5 × 10 ⁶
62. HNO ₂ + HNO ₃ → NO ₂ + NO ₂ + H ₂ O	8.2 × 10 ⁴
63. NO ₂ + NO ₃ → N ₂ O ₅	1.8 × 10 ⁹
64. N ₂ O ₅ → NO ₂ + NO ₃	1.5 × 10 ⁴
65. N ₂ O ₅ + H ₂ O → HNO ₃ + HNO ₃	2.5 × 10 ³
66. NO + NO ₃ → NO ₂ + NO ₂	6.0 × 10 ⁹

continued...

TABLE 7 (concluded)

Chemical Reaction				Rate Constant (at 120°C)
				(dm ³ ·mol ⁻¹ ·s ⁻¹)
67.	SO ₂	+ ·OH	→ HSO ₃	3.5 × 10 ⁸
68.	SO ₂	+ HO ₂	→ SO ₃ + ·OH	9.0 × 10 ⁵
69.	SO ₂	+ O·	→ SO ₃	4.0 × 10 ⁷
70.	SO ₃	+ H ₂ O	→ H ₂ SO ₄	5.5 × 10 ⁸
73.	HSO ₃	+ NO ₂	→ HSO ₅ N	5.0 × 10 ⁸
75.	HSO ₃	+ O ₂	→ HSO ₅	4.0 × 10 ⁸
78.	HSO ₅	+ NO	→ HSO ₄ + NO ₂	5.0 × 10 ⁹
79.	HSO ₅	+ NO	→ HSO ₆ N	5.0 × 10 ⁹
80.	HSO ₅	+ SO ₂	→ HSO ₄ + SO ₃	1.0 × 10 ⁹
81.	HSO ₄	+ NO	→ HSO ₅ N	1.0 × 10 ⁹

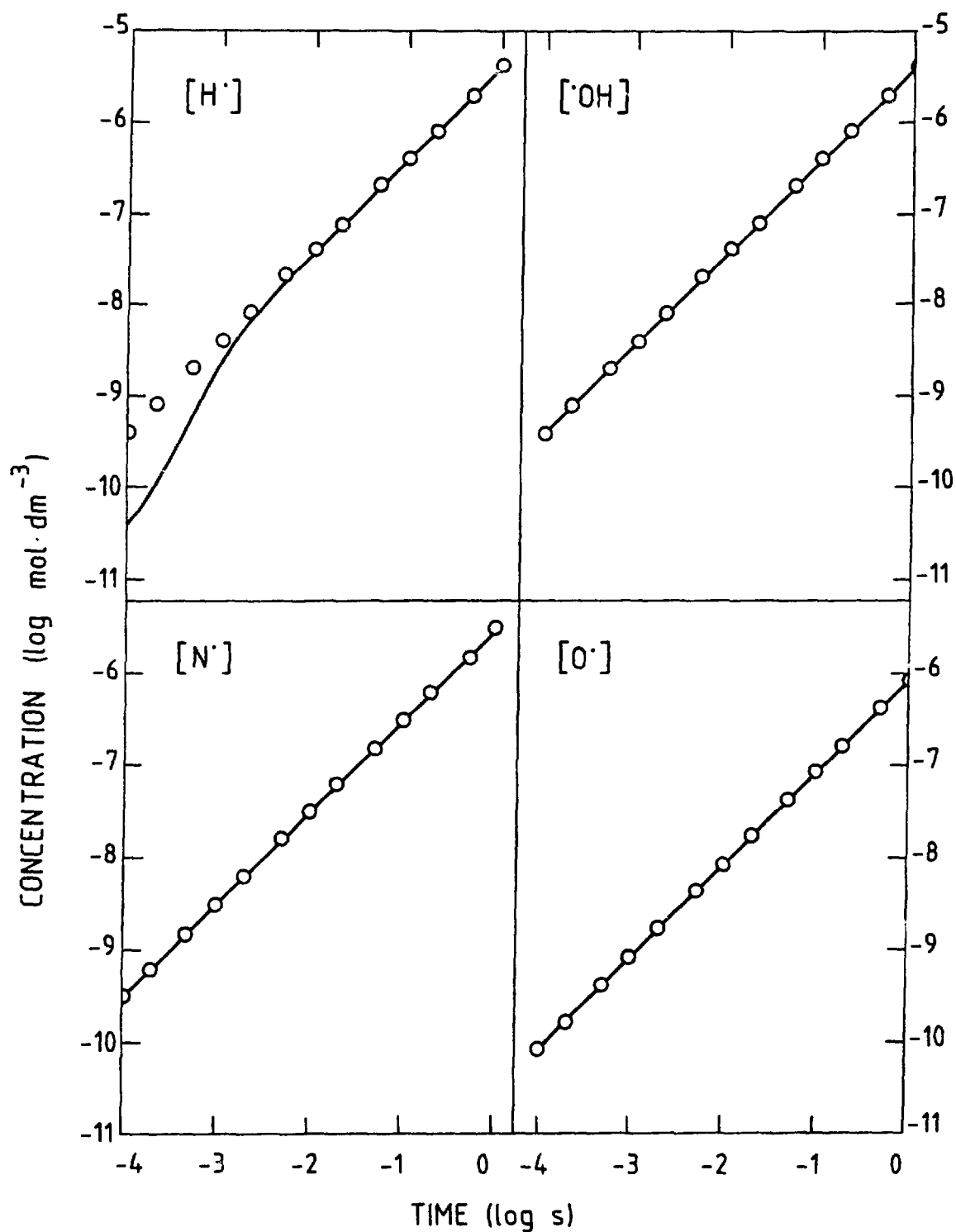


FIGURE 1: Comparison of Radical Concentrations as a Function of Time Predicted by the Full Radical Production Mechanism (Reaction 1 to 38 in Table 1) with Those Predicted by the Simplified Model (Table 4). The solid lines show the radical concentrations given by the full mechanism and the open circles show those given by the simplified model. Note that both concentration and time are plotted on logarithmic scales.

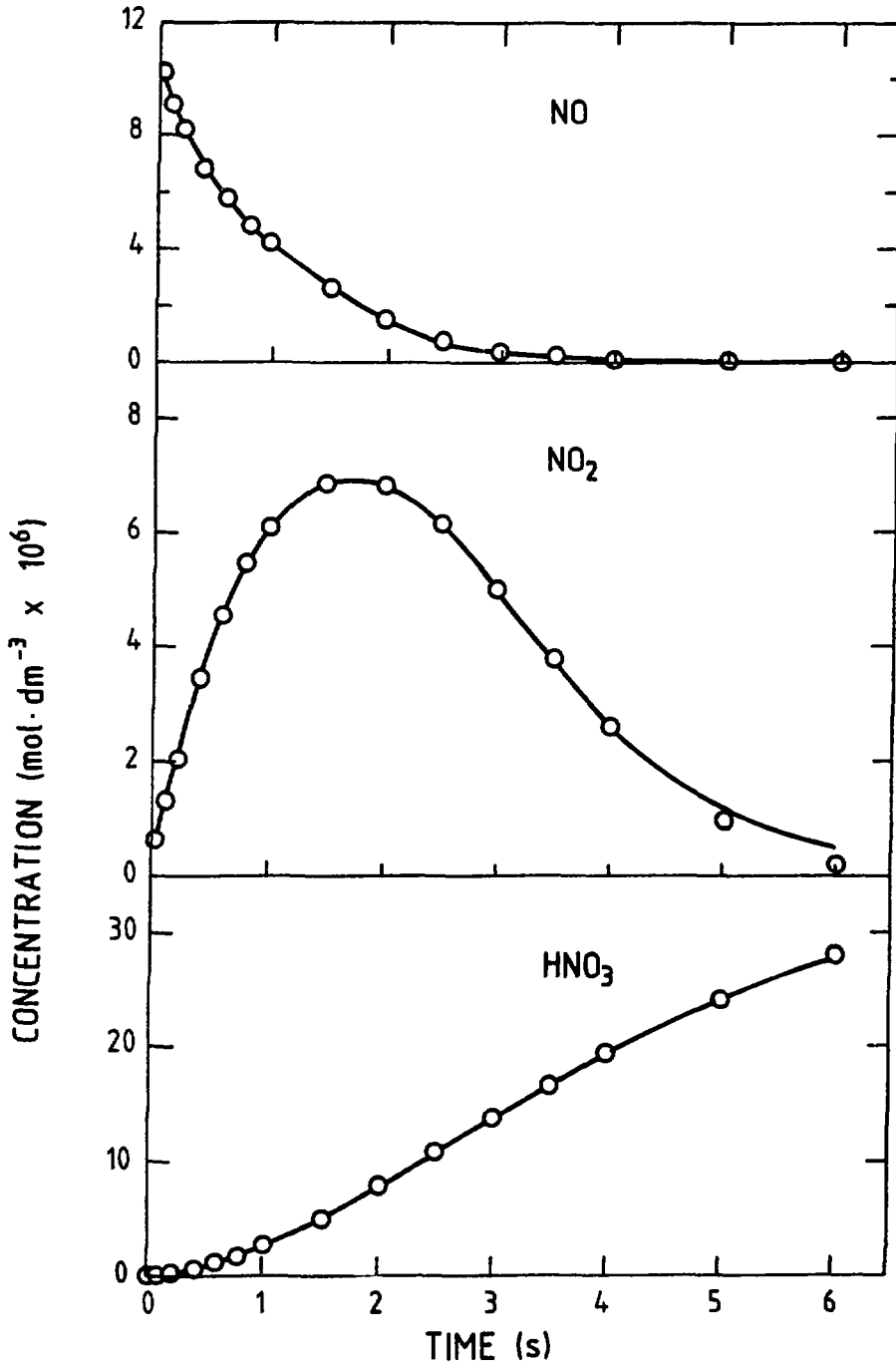


FIGURE 2: Comparison of NO, NO₂ and HNO₃ Concentrations Predicted by the Full NO_x Reaction Mechanism (Table 1) with Those Predicted by the Simplified Model (See Text) for the Radiation Treatment of a Combustion Flue Gas Initially Containing 68% N₂, 15.5% O₂, 10.5% H₂O, 6.0% CO₂, 250 ppm NO and 15 ppm NO₂ at a Dose Rate of 10 kGy · s⁻¹. The solid lines show the NO_x species concentrations given by the full mechanism and the open circles show those given by the simplified model.

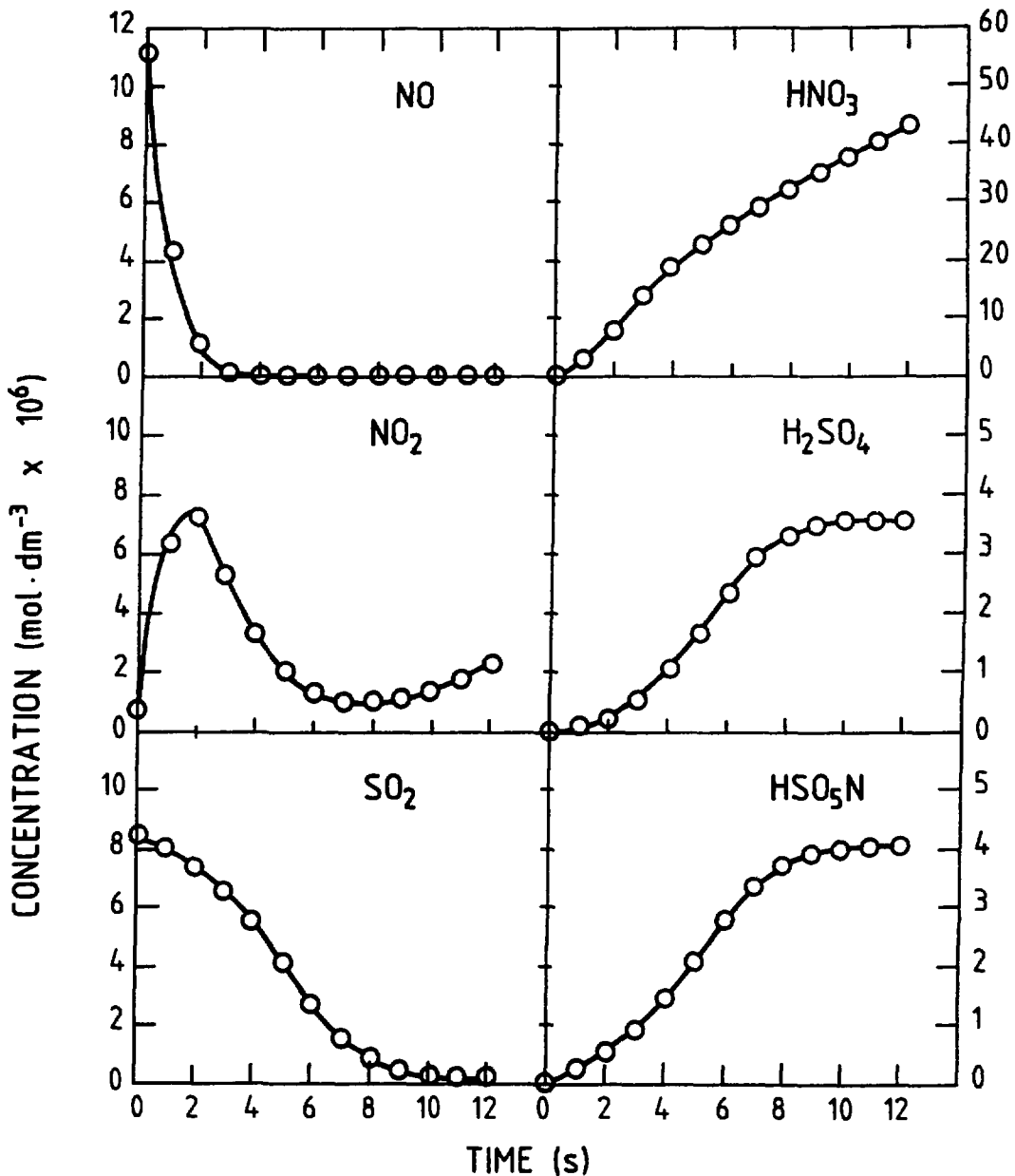


FIGURE 3. Comparison of NO, NO₂, HNO₃, SO₂, H₂SO₄ and HSO₅N Concentrations Predicted by the Full NO_x/SO₂ Reaction Mechanism (Tables 1 and 2) with Those Predicted by the Simplified Model (Tables 4 and 7) for the Radiation Treatment of a Combustion Flue Gas Initially Containing 68% N₂, 15.5% O₂, 10.5% H₂O, 6.0% CO₂, 250 ppm NO, 15 ppm NO₂ and 190 ppm SO₂ at a Dose Rate of 10 kGy · s⁻¹. The solid lines show the species concentrations given by the full mechanism and the open circles show those given by the simplified model.

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