

## MODELING AND SIMULATION OF OZONE FORMATION FROM A PROPENE-NITROGEN OXIDE-WET AIR MIXTURE IN A SMOG-CHAMBER

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**Abstract** – Ozone formation from a propene-nitrogen oxide-wet air mixture was modeled and simulated by using a detailed reaction model to characterize ozone formation in air pollution. Effects of reaction parameters such as light intensity, initial concentrations of propene and nitrogen oxides, temperature and humidity were investigated. The loss reactions of  $N_2O_5$  by  $H_2O$  were incorporated in the model developed in the present study. Results of simulations showed good agreement with smog-chamber experimental data. From the results of simulations it was found that the maximum ozone concentration was little affected by humidity. The model proposed in the present study can be used to predict the amount of ozone formation successfully.

**Key words:** *Ozone Formation, Propene, Nitrogen Oxides, Wet-Air Mixture, Modeling*

### INTRODUCTION

Often the most deleterious air pollutants are not emitted directly by sources but are those formed in the atmosphere by various chemical reactions. In an analysis of air pollution it is therefore necessary to understand the chemical reactions taking place in the atmosphere. The understanding of air pollution chemistry requires identification of the reactions contributing to the chemical dynamics. Thorough investigation of a specific reaction is achieved only when the reaction mechanism is properly specified. Because of the large number of important reactions that take place in the atmosphere, the rapid rates of many of them, and the low concentrations of most reactants, the experimental investigation of air pollution chemistry is very complex and difficult.

To characterize the formation of photochemical smog in air pollution, many recent attempts [Carter et al., 1979a, b; Sakamaki et al., 1982; Fan et al., 1996] have been made to correlate the maximum ozone concentration attained in smog-chamber experiments with the reaction parameters. It is well known that the formation of photochemical smog is influenced by a number of meteorological factors [Carter et al., 1979a, b; Seinfeld, 1986]. Their natural fluctuations contribute to the observed variation in the frequency and the intensity of episodes in different geographic locations and at different times of the year. There has been significant progress recently in understanding the dependences of the photochemical reaction parameters of elementary processes; however, no modeling and simulation experiments concerning the overall reaction parameters' dependence in ozone production have been conducted so far.

This study presents a reaction model which can characterize

ozone formation from a propene-nitrogen oxide-wet air mixture in terms of reaction parameters such as light intensity initial concentrations of propene and nitrogen oxide, temperature and humidity. The loss reactions of  $N_2O_5$  by  $H_2O$  were incorporated in the model developed in the present study. Since a detailed mechanism based on a knowledge of chemical kinetic data for the photooxidation in this system has been reported [Carter et al., 1979a; Sakamaki et al., 1982] recently, it is of great interest to determine whether computer modeling can reproduce the experimentally obtained relationship. For the purpose of establishing an ozone control strategy with the aid of computer simulation, a theoretical prediction is important. Results of simulations based on the reaction model developed in the present study showed good agreement with the experimental data.

### MODELING AND COMPUTATIONAL METHOD OF $C_3H_6-NO_x$ -WET AIR MIXTURE

#### 1. Reaction Mechanism

Photochemical reactions are initiated by the absorption of a photon by an atom, molecule, free radical or ion. The oxides of nitrogen, especially NO and  $NO_2$ , play an important role in air pollution chemistry. Most of the  $NO_x$  formed in combustion is NO. However,  $NO_2$  is formed to some extent from the NO in combustion exhaust gases by



Nitrogen dioxide is an important absorber of radiation at the wavelengths prevalent in the atmosphere. Even a small amount of  $NO_2$  present in the atmosphere is sufficient to trigger a complex series of reactions involving organics that lead to photochemical smog. Therefore,  $NO_2$  is the most important air pollutant molecule. When NO and  $NO_2$  are present in sunlight, ozone formation occurs as a result of the photolysis of

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NO<sub>2</sub>,

where M represents N<sub>2</sub> or O<sub>2</sub> or other third molecule that absorbs the excess vibrational energy and thereby stabilizes the O<sub>3</sub> molecule formed. There are no significant sources of ozone in the atmosphere other than reaction (3). Once formed, O<sub>3</sub> reacts with NO to regenerate NO<sub>2</sub>,



Sakamaki et al. [1982] have considered a dry air system at constant temperature. A wet-air system was considered in this present study, and so the loss reactions of N<sub>2</sub>O<sub>5</sub> by H<sub>2</sub>O were included in the model. For the simulation of ozone forma-

tion in the C<sub>3</sub>H<sub>6</sub>-NO<sub>x</sub>-wet air mixture according to temperature change, rate constants for the variable temperature were used in this study. The reaction of ozone with propene was postulated to give vibrationally stabilized biradicals (CH<sub>2</sub>OO and CH<sub>3</sub>CHOO) which react bimolecularly with NO, NO<sub>2</sub>, HCHO, and CH<sub>3</sub>CHO, and dioxiranes (CH<sub>2</sub>OO and CH<sub>3</sub>CHOO) which decompose or isomerize unimolecularly. The branching ratios of the unimolecular decay of CH<sub>2</sub>OO were taken from the study by Whitten et al. [1980]. The ratio of the atom and radical formation from CH<sub>3</sub>CHOO was decreased to 50 % of their values [Sakamaki et al., 1982]. The detailed reaction mechanism used in the present study is presented in Table 1. Assuming that known initial concentrations of C<sub>3</sub>H<sub>6</sub> and NO<sub>x</sub> are placed in a smog-chamber of constant volume, and treating O<sub>2</sub> and M as constant, the rate of the concentration change of O<sub>3</sub> after the irradiation begins is given by

Table 1. List of reactions and rate constants used in the C<sub>3</sub>H<sub>6</sub>-NO<sub>x</sub>-wet air system

Reaction no.	Reaction	Rate constant	Reference
1	NO <sub>2</sub> +hv → NO+O(P <sup>3</sup> )	1.0	a
2	O <sub>3</sub> +hv → O( <sup>1</sup> D)+O <sub>2</sub>	2.8×10 <sup>-3</sup>	a
3	→ O(P <sup>3</sup> ) + O <sub>2</sub>	2.0×10 <sup>-2</sup>	b
4	HONO+hv → OH+NO	1.5×10 <sup>-1</sup>	c
5	H <sub>2</sub> O <sub>2</sub> +hv → 2OH	4.9×10 <sup>-4</sup>	b
6	NO <sub>3</sub> +hv → NO+O <sub>2</sub>	4.3	d
7	→ NO <sub>2</sub> +O(P <sup>3</sup> )	1.3×10 <sup>1</sup>	d
8	HCHO+hv → H + HCO	2.0×10 <sup>-3</sup>	b
9	→ H <sub>2</sub> +CO	6.3×10 <sup>-3</sup>	b
10	CH <sub>3</sub> CHO+hv → CH <sub>3</sub> +HCO	2.6×10 <sup>-3</sup>	e
11	C <sub>2</sub> H <sub>5</sub> CHO+hv → C <sub>2</sub> H <sub>5</sub> +HCO	2.6×10 <sup>-3</sup>	b
12	CH <sub>3</sub> COCHO+hv → CH <sub>3</sub> C(O)O <sub>2</sub> +HCO	1.5×10 <sup>-1</sup>	b
13	CH <sub>3</sub> COCH <sub>2</sub> OH+hv → CH <sub>3</sub> C(O)O <sub>2</sub> +CH <sub>2</sub> OH	9.0×10 <sup>-4</sup>	b
14	CH <sub>3</sub> CH(OH)CHO+hv → CH <sub>3</sub> CHOH + HCO	2.6×10 <sup>-3</sup>	b
15	CH <sub>2</sub> CO+hv → CH <sub>2</sub> O <sub>2</sub> +CO	2.4×10 <sup>-3</sup>	b
16	→ CH <sub>2</sub> OO+CO	9.7×10 <sup>-3</sup>	b
17	CH <sub>3</sub> ONO+hv → CH <sub>3</sub> O+NO	1.3×10 <sup>-1</sup>	b
18	C <sub>2</sub> H <sub>5</sub> ONO+hv → C <sub>2</sub> H <sub>5</sub> O+NO	1.3×10 <sup>-1</sup>	b
19	O(P <sup>3</sup> )+O <sub>2</sub> +M → O <sub>3</sub> +M	6.0×10 <sup>-3</sup> (T/300) <sup>-2.3</sup>	a
20	O(3P)+NO <sub>2</sub> → NO+O <sub>2</sub>	9.3×10 <sup>-12</sup>	a
21	O(P <sup>3</sup> )+NO <sub>2</sub> +M → NO <sub>3</sub> +M	1.0×10 <sup>-31</sup>	b
22	O(P <sup>3</sup> )+NO+M → NO <sub>2</sub> +M	1.1×10 <sup>-31</sup>	b
23	O(P <sup>3</sup> )+O <sub>3</sub> → 2O <sub>2</sub>	9.6×10 <sup>-15</sup>	b
24	O( <sup>1</sup> D)+M → O(P <sup>3</sup> )+M	2.9×10 <sup>-11</sup>	a
25	O( <sup>1</sup> D)+H <sub>2</sub> O → 2OH	2.2×10 <sup>-10</sup>	a
26	O( <sup>1</sup> D)+O <sub>3</sub> → 2O <sub>2</sub>	2.4×10 <sup>-10</sup>	b
27	O <sub>3</sub> +NO → NO <sub>2</sub> +O <sub>2</sub>	2.2×10 <sup>-12</sup> exp(-1430/T)	a
28	O <sub>3</sub> +NO <sub>2</sub> → NO <sub>3</sub> +O <sub>2</sub>	1.2×10 <sup>-13</sup> exp(-2450/T)	a
29	O <sub>3</sub> +OH → HO <sub>2</sub> +O <sub>2</sub>	1.6×10 <sup>-12</sup> exp(-940/T)	a
30	O <sub>3</sub> +HO <sub>2</sub> → OH+2O <sub>2</sub>	3.1×10 <sup>-12</sup> exp(-187/T)	a
31	2NO+O <sub>2</sub> → 2NO <sub>2</sub>	3.3×10 <sup>-39</sup> exp(530/T)	a
32	NO+NO <sub>3</sub> → 2NO <sub>2</sub>	2.0×10 <sup>-11</sup>	a
33	NO+OH → HONO	6.6×10 <sup>-12</sup>	a
34	NO+HO <sub>2</sub> → OH+NO <sub>2</sub>	3.7×10 <sup>-12</sup> exp(240/T)	a
35	NO <sub>2</sub> +NO <sub>3</sub> → N <sub>2</sub> O <sub>5</sub>	4.7×10 <sup>-13</sup> exp(259/T)	a

Table 1. Continued

Reaction no.	Reaction	Rate constant	Reference
36	$\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3$	$2.0 \times 10^{14} \exp(-10660/T)$	a
37	$\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$	$1.1 \times 10^{-11}$	a
38	$\text{NO}_2 + \text{HO}_2 \rightarrow \text{HO}_2\text{NO}_2$	$1.4 \times 10^{-12}$	a
39	$\text{HO}_2\text{NO}_2 \rightarrow \text{HO}_2 + \text{NO}_2$	$1.3 \times 10^{14} \exp(-10418/T)$	a
40	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$[2.2 \times 10^{-13} \exp(620/T) + 1.9 \times 10^{-33} [\text{M}] \exp(980/T)] \times [1 + 1.4 \times 10^{-21} [\text{H}_2\text{O}] \exp(2200/T)]$	a
41	$\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{HO}_2 + \text{H}_2\text{O}$	$3.1 \times 10^{-12} \exp(-187/T)$	a
42	$\text{CO} + \text{OH} \rightarrow \text{H} + \text{CO}_2$	$3.0 \times 10^{-13}$	b
43	$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	$1.7 \times 10^{-32}$	b
44	$\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$	$4.4 \times 10^{-40}$	a
45	$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$	$2.0 \times 10^{-21}$	a
46	$\text{O}_3 \rightarrow \text{O}_3$ (wall)	$1.1 \times 10^{-5}$	b
47	$\text{NO}_2 \rightarrow \text{NO}_2$ (wall)	$7.2 \times 10^{-6}$	b
48	$\text{C}_3\text{H}_6 + \text{O}({}^3\text{P}) \rightarrow \text{C}_2\text{H}_5 + \text{HCO}$	$2.3 \times 10^{-12}$	b
49	$\rightarrow \text{CH}_3\text{CHCH}_2\text{O}$	$1.1 \times 10^{-12}$	b
50	$\rightarrow \text{C}_2\text{H}_5\text{CHO}$	$1.1 \times 10^{-12}$	b
51	$\text{HCO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO}$	fast	a
52	$\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2$	fast	b
53	$\text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{C}_2\text{H}_5\text{O}_2$	fast	b
54	$\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2$	$4.2 \times 10^{-12} \exp(180/T)$	a
55	$\text{C}_2\text{H}_5\text{O}_2 + \text{NO} \rightarrow \text{C}_2\text{H}_5\text{O} + \text{NO}_2$	$4.2 \times 10^{-12} \exp(180/T)$	a
56	$\text{CH}_3\text{O}_2 + \text{NO}_2 \rightarrow \text{CH}_3\text{O}_2\text{NO}_2$	$4.0 \times 10^{-12}$	a
57	$\text{CH}_3\text{O}_2\text{NO}_2 \rightarrow \text{CH}_3\text{O}_2 + \text{NO}_2$	$1.0 \times 10^1$	f
58	$\text{C}_2\text{H}_5\text{O}_2 + \text{NO}_2 \rightarrow \text{C}_2\text{H}_5\text{O}_2\text{NO}_2$	$1.3 \times 10^{-11}$	f
59	$\text{C}_2\text{H}_5\text{O}_2\text{NO}_2 \rightarrow \text{C}_2\text{H}_5\text{O}_2 + \text{NO}_2$	$1.0 \times 10^1$	f
60	$\text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{OOH} + \text{O}_2$	$2.9 \times 10^{-12}$	f
61	$\text{C}_2\text{H}_5\text{O}_2 + \text{HO}_2 \rightarrow \text{C}_2\text{H}_5\text{OOH} + \text{O}_2$	$2.9 \times 10^{-12}$	f
62	$2\text{CH}_3\text{O}_2 \rightarrow 2\text{CH}_3\text{O} + \text{O}_2$	$1.6 \times 10^{-13}$	b
63	$\rightarrow \text{CH}_3\text{OH} + \text{HCHO} + \text{O}_2$	$2.7 \times 10^{-13}$	b
64	$\rightarrow \text{CH}_3\text{OOCH}_3$	$3.0 \times 10^{-14}$	b
65	$2\text{C}_2\text{H}_5\text{O}_2 \rightarrow \text{C}_2\text{H}_5\text{OOC}_2\text{H}_5$	$4.5 \times 10^{-14}$	b
66	$\text{CH}_3\text{O} + \text{NO} \rightarrow \text{CH}_3\text{ONO}$	$1.7 \times 10^{-11}$	f
67	$\rightarrow \text{HCHO} + \text{HNO}$	$3.0 \times 10^{-12}$	f
68	$\text{C}_2\text{H}_5\text{O} \rightarrow \text{C}_2\text{H}_5\text{ONO}$	$1.7 \times 10^{-11}$	f
69	$\rightarrow \text{CH}_3\text{CHO} + \text{HNO}$	$3.0 \times 10^{-12}$	f
70	$\text{CH}_3\text{O} + \text{NO}_2 \rightarrow \text{CH}_3\text{ONO}_2$	$1.4 \times 10^{-11}$	f
71	$\rightarrow \text{HCHO} + \text{HNO}$	$2.4 \times 10^{-12}$	f
72	$\text{C}_2\text{H}_5\text{O} + \text{NO}_2 \rightarrow \text{C}_2\text{H}_5\text{ONO}_2$	$1.4 \times 10^{-11}$	f
73	$\rightarrow \text{CH}_3\text{CHO} + \text{HNO}$	$2.4 \times 10^{-12}$	f
74	$\text{CH}_3 + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2$	$6.8 \times 10^{-16}$	b
75	$\text{C}_2\text{H}_5\text{O} + \text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2$	$6.8 \times 10^{-16}$	b
76	$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO} \rightarrow \text{CH}_3 + \text{CO}_2 + \text{NO}_2$	$4.2 \times 10^{-12} \exp(180/T)$	a
77	$\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$	$4.7 \times 10^{-12}$	a
78	$\text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2$	$1.95 \times 10^{16} \exp(-13543/T)$	a
79	$\text{CH}_3\text{C}(\text{O})_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{O}_2\text{H} + \text{O}_2$	$3.0 \times 10^{-12}$	f
80	$\text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2 + \text{NO} \rightarrow \text{C}_2\text{H}_5 + \text{CO}_2 + \text{NO}_2$	$2.0 \times 10^{-11}$	f
81	$\text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2 + \text{NO}_2 \rightarrow \text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2\text{NO}_2$	$1.3 \times 10^{-11}$	f
82	$\text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2\text{NO}_2 \rightarrow \text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2 + \text{NO}_2$	$1.95 \times 10^{16} \exp(-13543/T)$	a
83	$\text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2 + \text{HO}_2 \rightarrow \text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2\text{H} + \text{O}_2$	$3.0 \times 10^{-12}$	f
84	$\text{C}_3\text{H}_6 + \text{O}_3 \rightarrow \text{CH}_3\text{CHO}_2^* + \text{HCHO}$	$5.5 \times 10^{-18}$	b
85	$\rightarrow \text{CH}_3\text{CHO} + \text{CH}_2\text{O}_2^*$	$5.5 \times 10^{-18}$	b
86	$\text{CH}_2\text{O}_2^* \rightarrow \text{CH}_2\text{O}_2$	(0.5)	b
87	$\rightarrow \text{CH}_2\text{OO}$	(0.5)	b
88	$\text{CH}_3\text{CHO}_2^* \rightarrow \text{CH}_3\text{CHO}_2$	(0.5)	b
89	$\rightarrow \text{CH}_3\text{CHO}$	(0.5)	b
90	$\text{CH}_2\text{O}_2 + \text{NO} \rightarrow \text{HCHO} + \text{NO}_2$	$1.9 \times 10^{-11}$	f
91	$\text{CH}_3\text{CHO}_2 + \text{NO} \rightarrow \text{CH}_3\text{CHO} + \text{NO}_2$	$1.9 \times 10^{-11}$	f

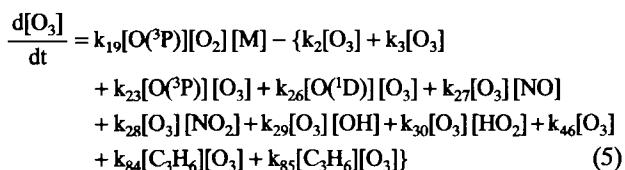
Table 1. Continued

Reaction no.	Reaction	Rate constant	Reference
92	CH <sub>2</sub> O <sub>2</sub> +NO <sub>2</sub> → HCHO+NO <sub>3</sub>	2.0×10 <sup>-12</sup>	g
93	CH <sub>3</sub> CHO <sub>2</sub> +NO <sub>2</sub> → CH <sub>3</sub> CHO+NO <sub>3</sub>	2.0×10 <sup>-12</sup>	g
94	CH <sub>2</sub> O <sub>2</sub> +HCHO → product	1.4×10 <sup>-13</sup>	b
95	CH <sub>2</sub> O <sub>2</sub> +CH <sub>3</sub> CHO → product	1.4×10 <sup>-13</sup>	b
96	CH <sub>3</sub> CHO <sub>2</sub> +HCHO → product	7.0×10 <sup>-13</sup>	adj
97	CH <sub>3</sub> CHO <sub>2</sub> +CH <sub>3</sub> CHO → product	7.0×10 <sup>-13</sup>	adj
98	CH <sub>2</sub> OO → H <sub>2</sub> +CO <sub>2</sub>	(0.18)	b
99	→ CO+H <sub>2</sub> O	(0.67)	b
100	→ 2H+CO <sub>2</sub>	(0.09)	b
101	→ HCHO	(0.06)	b
102	CH <sub>3</sub> CHOO → CH <sub>4</sub> +CO <sub>2</sub>	(0.24)	b
103	→ CH <sub>3</sub> +CO+OH	(0.27)	b
104	→ CH <sub>3</sub> +H+CO <sub>2</sub>	(0.35)	b
105	→ CH <sub>3</sub> O+H+CO	(0.06)	b
106	→ CH <sub>2</sub> CO+H <sub>2</sub> O	(0.08)	b
107	C <sub>3</sub> H <sub>6</sub> +OH $\xrightarrow{O_2}$ CH <sub>3</sub> CH(O <sub>2</sub> )CH <sub>2</sub> OH	1.6×10 <sup>-11</sup>	f
108	C <sub>3</sub> H <sub>6</sub> +OH $\xrightarrow{O_2}$ CH <sub>3</sub> CH(O <sub>2</sub> )CH <sub>2</sub> OH	8.6×10 <sup>-12</sup>	f
109	CH <sub>3</sub> CH(O <sub>2</sub> )CH <sub>2</sub> OH+NO → CH <sub>3</sub> CH(O)CH <sub>2</sub> OH+NO <sub>2</sub>	1.9×10 <sup>-11</sup>	f
110	→ CH <sub>3</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> OH	3.6×10 <sup>-13</sup>	adj
111	CH <sub>3</sub> CH(OH)CH <sub>2</sub> O <sub>2</sub> +NO → CH <sub>3</sub> CH(OH)CH <sub>2</sub> O+NO <sub>2</sub>	1.9×10 <sup>-11</sup>	f
112	→ CH <sub>3</sub> CH(OH)CH <sub>2</sub> ONO <sub>2</sub>	3.6×10 <sup>-13</sup>	adj
113	CH <sub>3</sub> CH(O <sub>2</sub> )CH <sub>2</sub> OH+NO <sub>2</sub> → CH <sub>3</sub> CH(O <sub>2</sub> NO <sub>2</sub> )CH <sub>2</sub> OH	1.3×10 <sup>-11</sup>	f
114	CH <sub>3</sub> CH(O <sub>2</sub> NO <sub>2</sub> )CH <sub>2</sub> OH → CH <sub>3</sub> CH(O <sub>2</sub> )CH <sub>2</sub> OH+NO <sub>2</sub>	1.0×10 <sup>1</sup>	f
115	CH <sub>3</sub> CH(OH)CH <sub>2</sub> O <sub>2</sub> +NO <sub>2</sub> → CH <sub>3</sub> CH(OH)CH <sub>2</sub> O <sub>2</sub> NO <sub>2</sub>	1.3×10 <sup>-11</sup>	f
116	CH <sub>3</sub> CH(OH)CH <sub>2</sub> O <sub>2</sub> NO <sub>2</sub> → CH <sub>3</sub> CH(OH)CH <sub>2</sub> O <sub>2</sub> +NO <sub>2</sub>	1.0×10 <sup>1</sup>	f
117	CH <sub>3</sub> CH(O)CH <sub>2</sub> OH → CH <sub>3</sub> CHO+CH <sub>2</sub> OH	2.3×10 <sup>6</sup>	adj
118	CH <sub>3</sub> C(OH)CH <sub>2</sub> O → CH <sub>3</sub> CHOH+HCHO	4.0×10 <sup>5</sup>	adj
119	CH <sub>2</sub> OH+O <sub>2</sub> → HCHO+HO <sub>2</sub>	fast	b
120	CH <sub>3</sub> CHOH+O <sub>2</sub> → CH <sub>3</sub> CHO+HO <sub>2</sub>	fast	b
121	CH <sub>3</sub> CH(O)CH <sub>2</sub> OH+O <sub>2</sub> → CH <sub>3</sub> C(O)CH <sub>2</sub> OH+HO <sub>2</sub>	1.2×10 <sup>-15</sup>	f
122	CH <sub>3</sub> CH(OH)CH <sub>2</sub> O+O <sub>2</sub> → CH <sub>3</sub> CH(OH)CHO+HO <sub>2</sub>	1.2×10 <sup>-15</sup>	f
123	CH <sub>3</sub> CH(O <sub>2</sub> )CH <sub>2</sub> OH+HO <sub>2</sub> → CH <sub>3</sub> CH(O <sub>2</sub> H)CH <sub>2</sub> OH+O <sub>2</sub>	2.9×10 <sup>-12</sup>	f
124	CH <sub>3</sub> CH(OH)CH <sub>2</sub> O <sub>2</sub> +HO <sub>2</sub> → CH <sub>3</sub> CH(OH)CH <sub>2</sub> O <sub>2</sub> H+O <sub>2</sub>	2.9×10 <sup>-12</sup>	f
125	CH <sub>3</sub> C(O)CH <sub>2</sub> OH+OH → CH <sub>3</sub> C(O)CHOH+H <sub>2</sub> O	7.0×10 <sup>-12</sup>	f
126	CH <sub>3</sub> C(O)CHOH+O <sub>2</sub> → CH <sub>3</sub> C(O)CHO+HO <sub>2</sub>	fast	b
127	CH <sub>3</sub> CH(OH)CHO+OH → CH <sub>3</sub> C(OH)CHO+H <sub>2</sub> O	1.3×10 <sup>-11</sup>	f
128	CH <sub>3</sub> C(OH)CHO+O <sub>2</sub> → CH <sub>3</sub> C(O)CHO+HO <sub>2</sub>	fast	b
129	CH <sub>3</sub> CH(OH)CHO+OH → CH <sub>3</sub> CH(OH)CO+H <sub>2</sub> O	1.6×10 <sup>-11</sup>	f
130	CH <sub>3</sub> CH(OH)CO+O <sub>2</sub> → CH <sub>3</sub> CH(OH)C(O)O <sub>2</sub>	fast	b
131	CH <sub>3</sub> CH(OH)C(O)O <sub>2</sub> +NO → CH <sub>3</sub> CH(OH)CO <sub>2</sub> +NO <sub>2</sub>	2.0×10 <sup>-11</sup>	f
132	CH <sub>3</sub> CH(OH)CO <sub>2</sub> → CH <sub>3</sub> CHOH+CO <sub>2</sub>	fast	b
133	CH <sub>3</sub> CH(OH)C(O)O <sub>2</sub> +NO <sub>2</sub> → CH <sub>3</sub> CH(OH)C(O)O <sub>2</sub> NO <sub>2</sub>	1.3×10 <sup>-11</sup>	f
134	CH <sub>3</sub> CH(OH)C(O)O <sub>2</sub> NO <sub>2</sub> → CH <sub>3</sub> CH(OH)C(O)O <sub>2</sub> +NO <sub>2</sub>	8.0×10 <sup>-4</sup>	f
135	CH <sub>3</sub> C(O)CHO+OH → CH <sub>3</sub> C(O)CO+H <sub>2</sub> O	1.6×10 <sup>-11</sup>	f
136	CH <sub>3</sub> C(O)CO → CH <sub>3</sub> CO+CO	fast	b
137	C <sub>3</sub> H <sub>6</sub> +NO <sub>3</sub> $\xrightarrow{O_2}$ CH <sub>3</sub> CH(O <sub>2</sub> )CH <sub>2</sub> ONO <sub>2</sub>	5.5×10 <sup>-15</sup>	f
138	→ CH <sub>3</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> O <sub>2</sub>	2.7×10 <sup>-15</sup>	f
139	CH <sub>3</sub> CH(O <sub>2</sub> )CH <sub>2</sub> ONO <sub>2</sub> +NO → CH <sub>3</sub> CH(O)CH <sub>2</sub> ONO <sub>2</sub> +NO <sub>2</sub>	1.9×10 <sup>-11</sup>	f
140	→ CH <sub>3</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> ONO <sub>2</sub>	3.6×10 <sup>-12</sup>	adj
141	CH <sub>3</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> O <sub>2</sub> +NO → CH <sub>3</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> O+NO <sub>2</sub>	1.9×10 <sup>-11</sup>	f
142	→ CH <sub>3</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> ONO <sub>2</sub>	3.6×10 <sup>-12</sup>	adj
143	CH <sub>3</sub> CH(O <sub>2</sub> )CH <sub>2</sub> ONO <sub>2</sub> +NO <sub>2</sub> → CH <sub>3</sub> CH(O <sub>2</sub> NO <sub>2</sub> )CH <sub>2</sub> ONO <sub>2</sub>	1.3×10 <sup>-11</sup>	f
144	CH <sub>3</sub> CH(O <sub>2</sub> NO <sub>2</sub> )CH <sub>2</sub> ONO <sub>2</sub> → CH <sub>3</sub> CH(O <sub>2</sub> )CH <sub>2</sub> ONO <sub>2</sub> +NO <sub>2</sub>	1.0×10 <sup>1</sup>	f
145	CH <sub>3</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> O <sub>2</sub> +NO <sub>2</sub> → CH <sub>3</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> O <sub>2</sub> NO <sub>2</sub>	1.3×10 <sup>-11</sup>	f

Table 1. Continued

Reaction no.	Reaction	Rate constant	Reference
146	$\text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_2\text{O}_2\text{NO}_2 \rightarrow \text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_2\text{O}_2+\text{NO}_2$	$1.0 \times 10^{-1}$	f
147	$\text{CH}_3\text{CH}(\text{O}_2)\text{CH}_2\text{ONO}_2+\text{HO}_2 \rightarrow \text{CH}_3\text{CH}(\text{OOH})\text{CH}_2\text{ONO}_2+\text{O}_2$	$2.9 \times 10^{-12}$	f
148	$\text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_2\text{O}+\text{HO}_2 \rightarrow \text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_2\text{OOH}+\text{O}_2$	$2.9 \times 10^{-12}$	f
149	$\text{CH}_3\text{CH}(\text{O})\text{CH}_2\text{ONO}_2+\text{NO}_2 \rightarrow \text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_2\text{ONO}_2$	$1.4 \times 10^{-11}$	f
150	$\text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_2\text{O}+\text{NO}_2 \rightarrow \text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_2\text{ONO}_2$	$1.4 \times 10^{-11}$	f
151	$\text{CH}_3\text{CH}(\text{O})\text{CH}_2\text{ONO}_2+\text{O}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{ONO}_2+\text{H}_2\text{O}$	$3.0 \times 10^{-18}$	b
152	$\text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_2\text{O}+\text{O}_2 \rightarrow \text{CH}_3\text{CH}(\text{ONO}_2)\text{CHCHO}+\text{HO}_2$	$3.0 \times 10^{-18}$	b
153	$\text{CH}_3\text{CH}(\text{O})\text{CH}_2\text{ONO}_2 \rightarrow \text{CH}_3\text{CHO}+\text{HCHO}+\text{NO}_2$	$3.1 \times 10^5$	b
154	$\text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_2\text{O} \rightarrow \text{CH}_3\text{CHO}+\text{HCHO}+\text{NO}_2$	$3.0 \times 10^1$	b
155	$\text{HCHO}+\text{OH} \rightarrow \text{HCO}+\text{H}_2\text{O}$	$9.4 \times 10^{-12}$	f
156	$\text{CH}_3\text{CHO}+\text{OH} \xrightarrow{\text{O}_2} \text{CH}_3\text{CO}(\text{O}_2)+\text{H}_2\text{O}$	$1.6 \times 10^{-11}$	f
157	$\text{C}_2\text{H}_5\text{CHO}+\text{OH} \xrightarrow{\text{O}_2} \text{C}_2\text{H}_5\text{CO}(\text{O}_2)+\text{H}_2\text{O}$	$1.6 \times 10^{-11}$	f
158	$\text{HCHO}+\text{NO}_3 \rightarrow \text{HCO}+\text{HNO}_3$	$1.8 \times 10^{-15}$	f
159	$\text{CH}_3\text{CHO}+\text{NO}_3 \xrightarrow{\text{O}_2} \text{CH}_3\text{CO}(\text{O}_2)+\text{HNO}_3$	$2.0 \times 10^{-15}$	f
160	$\text{C}_2\text{H}_5\text{CHO}+\text{NO}_3 \xrightarrow{\text{O}_2} \text{C}_2\text{H}_5\text{CO}(\text{O}_2)+\text{HNO}_3$	$2.0 \times 10^{-15}$	f

a: Seinfeld, 1986, b: Sakamaki et al., 1982, c: Stockwell and Calvert, 1978, d: Graham and Johnston, 1978, e: Weaver et al., 1977, f: Carter et al., 1979a, g: Whitten et al., 1977, adj: adjust



The dynamic equations for the other reactants can be written, just as we have done for  $\text{O}_3$ . In Table 1 the values in parentheses are branching ratios normalized to unity and the photolysis rate constants are the relative rates to that of  $\text{NO}_2$ . The mechanisms presented in Table 1 are based on those reported by Sakamaki et al. [1982] with some modifications.

## 2. Smog-Chamber Experiments and Computational Method

The experimental facilities and methods employed in these smog chamber experiments are discussed in detailed elsewhere [Carter et al., 1979b; Sakamaki et al., 1982] and are only briefly described here. The evacuable thermostated chamber consists of a 5800-L cylindrical aluminum alloy cell coated on the inside with Teflon and equipped with quartz end windows. Photolysis was performed with a 25000 W solar simulator producing a collimated beam designed to minimize direct irradiation of the chamber walls. The temperature control system was designed to regulate the temperature of chamber walls to  $\pm 0.5^\circ\text{C}$  over the  $-20$  to  $+100^\circ\text{C}$  range. In this system ethylene glycol is heated or cooled by external heat exchangers and then circulated by means of a 1.5 hp pump through channels welded to the chamber exterior. A 10-kW electrical heater powers the exchanger used for the heating cycle, and a 7.5-ton two-stage refrigeration unit is used for the cooling cycle. The chamber walls are insulated with 1 in. of fiberglass insulation and 2 in. of polyurethane foam and are covered with an aluminum sheath. Prior to each experiment, the chamber was evacuated to at least  $10^{-4}$  Torr. After the chamber was filled with purified matrix air [Carter et al., 1979b] at the de-

sired temperature and relative humidity, reactants were added and allowed to mix for at least 30 min. Ozone,  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{NO}_x$  were monitored by chemiluminescence method, and  $\text{CO}$  and organics by gas chromatography.

For computation the concentration of water vapor must be in units of ppm. For a given ambient temperature  $T$ , relative humidity  $\text{RH}$  is defined as the ratio of the partial pressure of water to its saturation vapor pressure at the same temperature. Alternatively,  $\text{RH}$  is the ratio of the actual mole fraction of water vapor  $y$  to that at saturation,  $y_s$ ,

$$\text{RH} = 100 \frac{y}{y_s} \quad (6)$$

where the factor 100 is used because  $\text{RH}$  is usually expressed in percent. Since the mole fraction is equivalent to the volume fraction, the water concentration in ppm is given by

$$[\text{H}_2\text{O}] = 10^6 y = 10^4 \text{RH } y_s \text{ (ppm)} \quad (7)$$

This equation can be written in terms of  $p_{\text{H}_2\text{O}}^0$  and the atmospheric pressure  $p$ ,

$$[\text{H}_2\text{O}] = 10^4 \text{RH} \frac{p_{\text{H}_2\text{O}}^0}{p} \text{ (ppm)} \quad (8)$$

In order to evaluate this expression, the saturation vapor pressure must be known. McRae [1980] suggested the following expression for  $p_{\text{H}_2\text{O}}^0$ :

$$p_{\text{H}_2\text{O}}^0(T) = p_s \exp [13.3185a - 1.9760a^2 - 0.6445a^3 - 0.1299a^4] \quad (9)$$

where  $p_s$  is the standard atmospheric pressure of 1013.25 mb, and the parameter  $a$  is defined in terms of the ambient  $T(\text{K})$  and the steam temperature  $T_s = 373.15 \text{ K}$  at  $p_s$ ,

$$a = 1 - \frac{T_s}{T} = \frac{T - 373.15}{T} \quad (10)$$

The experimental data presented by Sakamaki et al. [1982] and Carter et al. [1979b] were used to evaluate the results of simulations based on the present reaction models. Curve fitting of the experimental data and the simulation results was attempted for the  $C_3H_6$  (3.05 ppm)-NO (1.477 ppm)- $NO_2$  (0.023 ppm)-dry air run. Fitting to the time profiles of NO,  $NO_2$ ,  $C_3H_6$  and  $O_3$ , as well as to the maximum  $O_3$  level, was attempted as a first priority. The trials were made by adjusting the reaction rate constant. Calculations were performed on an IBM PC 586 computer by using the 4th Runge-Kutta method for the integration of coupled differential equations.

## RESULTS AND DISCUSSION

The initial conditions for each simulation are given in Table 2 together with experimental and simulated results for  $[O_3]_{max}$ . Fig. 1 shows the time profile of each species simulated using the present reaction model for the  $C_3H_6$  (3.05 ppm)-NO (1.477 ppm)- $NO_2$  (0.023 ppm)-dry air run. Initial conditions used for the simulation are the same as those for the experiment. A slight discrepancy in the simulation as compared to the experimental data can be noted in Fig. 1. Such a discrepancy was reported as a result of the unknown radical source of OH and  $HO_2$  [Carter et al., 1979a]. However, in this study, the hypothetical radical source was not included since there was little discrepancy between the simulation and the experiment. A comparison of  $[O_3]_{max}$  in the  $C_3H_6$ - $NO_x$ -wet air mixture obtained by simulations and experiments according to  $[C_3H_6]_0$ ,  $[NO_x]_0$ ,  $k_1$ , and humidity is shown in Table 2 and Figs. 2-5. Fig. 2 shows that the  $[O_3]_{max}$  increases when  $[NO_x]_0$  is increased, keeping  $[C_3H_6]_0$  constant, and there is little discrepancy between the

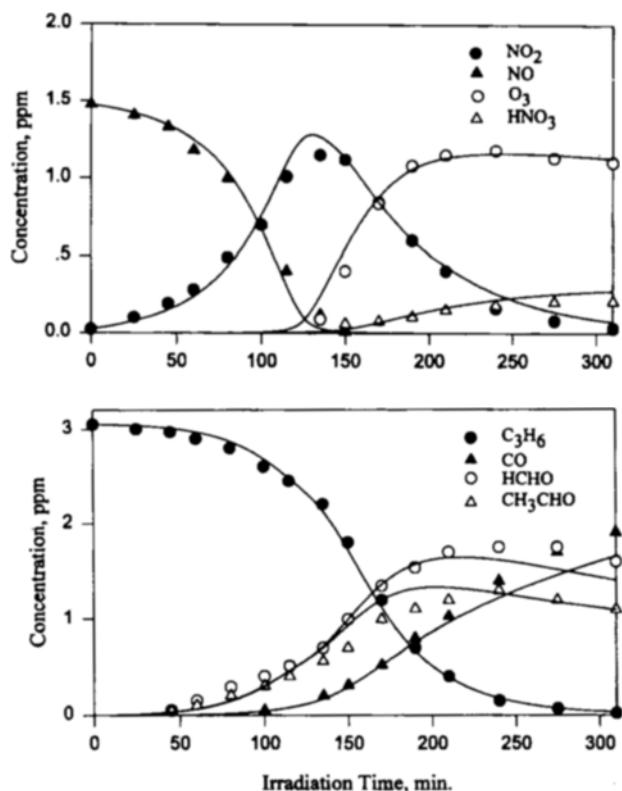


Fig. 1. The comparison of simulated (lines) and experimental (symbols) concentrations for the  $C_3H_6$ - $NO_x$ -wet air system, run no. 1 in Table 2.

simulation and the experiment. In Fig. 3, it was found that the  $[O_3]_{max}$  could be calculated according to  $[C_3H_6]_0$ , although

Table 2. Experimental and simulated results for Irradiation of the  $C_3H_6$ - $NO_x$ -wet air System

Run no.	Temp. (°C)	Run conditions				Light inten. $k_1, min^{-1}$	RH %	Experimental $[O_3]_{max}$ , ppm	Calculated $[O_3]_{max}$ , ppm
		$C_3H_6$	Initial concn., ppm	NO	$NO_2$				
1	30	3.05	1.477	0.023	0.27	dry air	1.180	1.161	
2	30	0.50	0.004	0.041	0.16	dry air	0.151	0.145	
3	30	0.50	0.008	0.082	0.16	dry air	0.236	0.236	
4	30	0.50	0.011	0.176	0.16	dry air	0.363	0.367	
5	30	0.50	0.255	0.035	0.16	dry air	0.443	0.463	
6	30	0.05	0.003	0.035	0.16	dry air	0.085	0.105	
7	30	0.20	0.004	0.036	0.16	dry air	0.136	0.129	
8	30	0.30	0.005	0.034	0.16	dry air	0.136	0.138	
9	30	0.40	0.005	0.035	0.16	dry air	0.139	0.141	
10	30	0.50	0.012	0.073	0.37	dry air	0.390	0.372	
11	30	0.50	0.012	0.078	0.31	dry air	0.366	0.359	
12	30	0.50	0.009	0.074	0.25	dry air	0.307	0.311	
13	30	0.50	0.009	0.079	0.19	dry air	0.271	0.284	
14	30	0.50	0.007	0.082	0.13	dry air	0.232	0.235	
15	30	0.10	0.004	0.032	0.16	dry air	0.106	0.130	
16	30	0.10	0.004	0.032	0.16	20	-	0.130	
17	30	0.10	0.004	0.032	0.16	40	-	0.129	
18	30	0.10	0.004	0.032	0.16	60	-	0.128	
19	16.1	9.50	3.960	1.880	0.38	11	2.340	2.388	
20	32.8	10.1	4.150	1.880	0.38	5.0	2.423	2.395	
21	50.5	10.64	4.740	1.870	0.39	2.0	2.050	2.116	

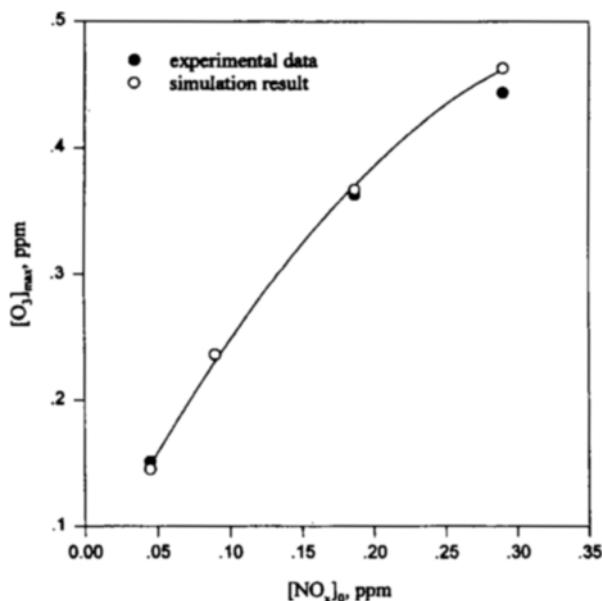


Fig. 2. The comparison of simulated and experimental  $[O_3]_{max}$  for the change of  $[NO_x]_0$ , run no. 2, 3, 4 and 5 in Table 2.

there is a slight disagreement between the simulation and experiment which might be due to the experimental error in the low-concentration runs. Fig. 4 shows a comparison of simulated and experimental  $[O_3]_{max}$  when the light intensity,  $k_1$ , is changed keeping  $[C_3H_6]_0$ ,  $[NO_x]_0$  constant. As can be seen, the proportional relationship between the  $[O_3]_{max}$  and  $k_1$  has been well reproduced. Fig. 5 shows the results of simulations for the change of humidity. From the results of simulations it was found that the rates of  $O_3$  formation increase with increasing humidity, but the  $[O_3]_{max}$  concentration was little affected by humidity. Although the experimental data were in-

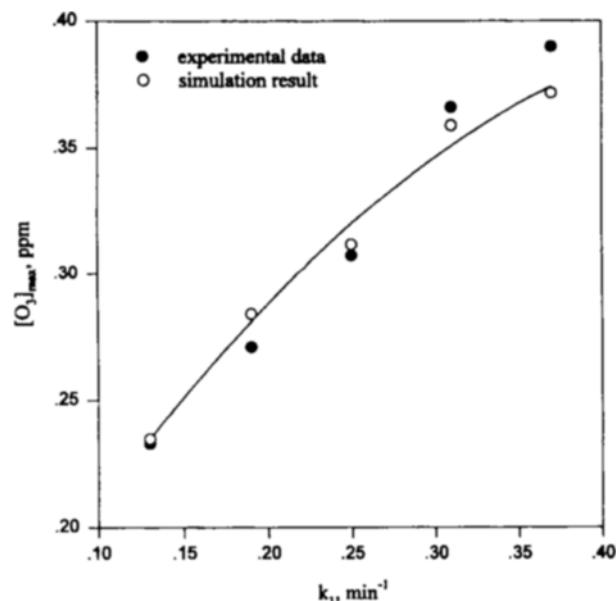


Fig. 4. The comparison of simulated and experimental  $[O_3]_{max}$  for the change of light intensity, run no. 10, 11, 12, 13 and 14 in Table 2.

sufficient to determine whether the variation in humidity has a significant effect, preliminary results of simulation performed in this work suggest that humidity effects are small compared to those of the other reaction parameters, at least for the propene-nitrogen oxide-wet air mixture. Fig. 6 shows the time profiles of  $O_3$  simulated using the present reaction model for the change of temperature,  $T \geq 16^\circ C$ . From Fig. 6 we can see that the rates of  $O_3$  formation increase with increasing temperature, while the  $[O_3]_{max}$  concentration was relatively unaffected by temperature. The rate of formation of  $O_3$  could not be predicted precisely by the present model due to insufficient experimental kinetic data. But the computed concentration of

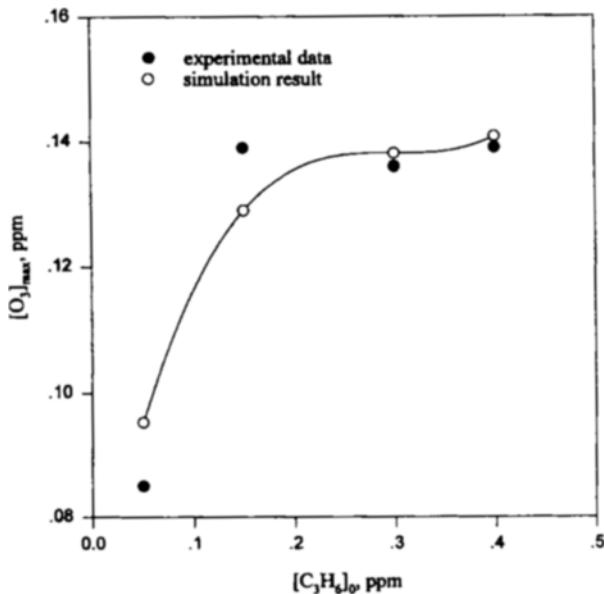


Fig. 3. The comparison of simulated and experimental  $[O_3]_{max}$  for the change of  $[C_3H_6]_0$ , run no. 6, 7, 8 and 9 in Table 2.

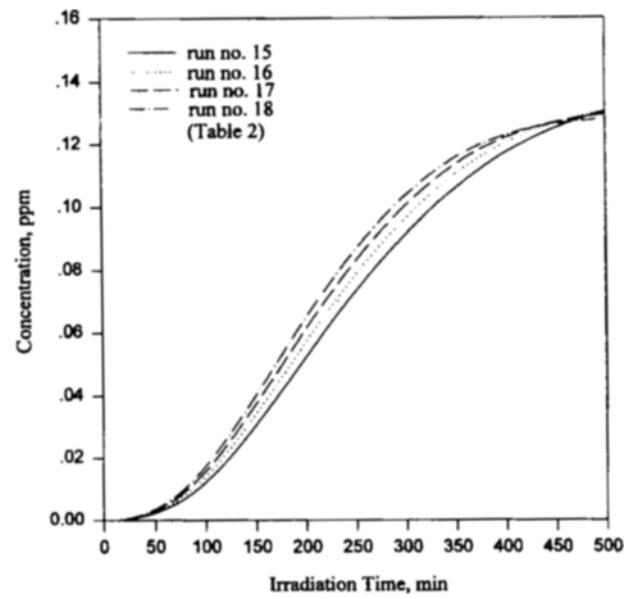


Fig. 5. The simulation results of the rates of  $O_3$  formation for the change of humidity.

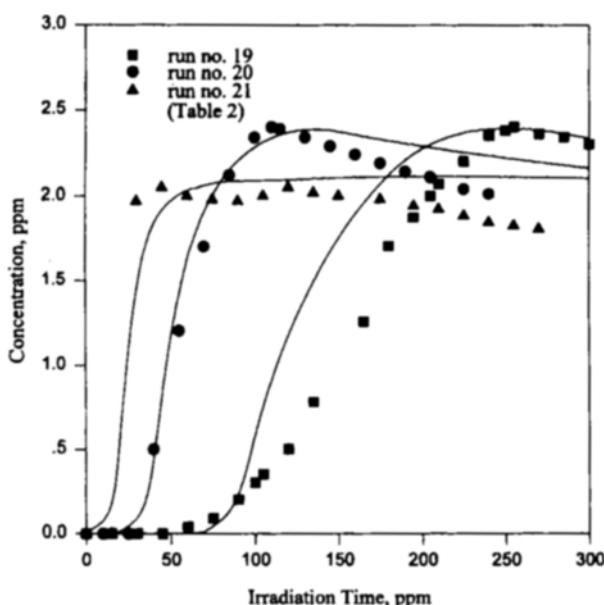


Fig. 6. The comparison of simulated (lines) and experimental (symbols) rates of  $O_3$  formation for the change of temperature.

$[O_3]_{max}$  showed good agreement with the experimental value.

### CONCLUSION

The modeling and simulation of the  $C_3H_6$ -NO<sub>x</sub>-wet air mixture was performed by using a detailed reaction model considering the effect of temperature and the loss reactions of  $N_2O_5$  by  $H_2O$  in order to characterize  $O_3$  formation in air pollution. From the results of simulations it was found that the reaction model developed in the present study can be used to predict the amounts of  $O_3$  formation successfully. Although the photochemical models presented in this study took into account the effects of temperature and humidity on photochemical ozone formation, the predictive capabilities of the models concerning these effects do not appear to be totally satisfactory, and they may have errors in important areas relating to

temperature effects. Further basic studies of the temperature and humidity dependences of the photochemical reaction mechanisms are required to improve the effectiveness of the photochemical models.

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