Aug 84

10 DOWNING STREET

From the Private Secretary

6 June, 1984

Acid Rain

I am writing on behalf of the Prime Minister to thank you for your letter of 5 June, and the formidable list of chemical reactions which you enclosed. I will show this to the Prime Minister over the weekend, and I know she will be interested (as well as impressed) by it.

DAVID BARCLAY

Dr. P. F. Chester

CT.

(cf PPS RLO)

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The Prime Minister
10 Downing Street
Whitehall,
London, SW1

Our ref RL/PFC/DSL
06/05/01.3

Your ref

Date 5 June 1984

Dear Prime Minister,

Chemical Reactions Producing Acid Rain

At the meeting at Chequers on 27 May you said you would like to see a list of the chemical reactions involved in the formation of acid rain. Diagram 6 of my Presentation involved the 93 reactions listed in the attachment. Of these the fifteen marked "**" are the vital steps in the formation of photochemical oxidants.

A glance at the list will give you some idea of the complexity of the processes involved and the role played by hydrocarbons.

Yours sincerely,

Peter Chester

P.F. Chester
Research Director

cc: Sir Walter Marshall
Dr. Robin Nicholson, Cabinet Office

REACTIONS USED IN CERL ATMOSPHERIC ACIDITY MODEL

(Diagram 6 presented on 27.5.84)

Those marked ** are important for the formation of photochemical oxidants.

Those marked N make a negligible contribution to overall result.

Table 6

	Reaction	Rate Constant[a]
1.	$NO + O_3 \rightarrow NO_2 + O_2$	$51.7 \exp(-1450/T)$
N. 2.	$2NO + O_2 \rightarrow 2NO_2$	$2.0 \times 10^{-12} \exp(530/T)$
** 3.	$NO_2 + h\nu \rightarrow NO + O$	7.8×10^{-3} s^{-1} [b]
** 4.	$O + O_2 + M \rightarrow O_3 + M$	$6.47 \times 10^{-2} \exp(510/T)$
N. 5.	$O + NO_2 \rightarrow NO + O_2$	2.2×10^2
N. 6.	$O + NO + M \rightarrow NO_2 M$	$9.38 \exp(584/T)$
N. 7.	$O + NO_2 + M \rightarrow NO_3 + M$	61
8.	$NO_3 \quad h\nu \rightarrow NO_2 + O$	9.9×10^{-2} s^{-1} [b]
9.	$NO_3 + h\nu \rightarrow NO + O_2$	4.0×10^{-2} s^{-1} [b]
10.	$NO_3 + NO \rightarrow 2NO_2$	4.6×10^2
11.	$NO_2 + O_3 \rightarrow NO_3 + O_2$	$2.95 \exp(-2450/T)$
N. 12.	$O_3 + h\nu \rightarrow O_2 + O$	5.1×10^{-4} s^{-1} [b]
** 13.	$O_3 + h\nu \rightarrow O_2 + O(^1D_2)$	3.2×10^{-5} s^{-1} [b]
14.	$O(^1D_2) + M \rightarrow O + M$	$4.92 \times 10^8 \exp(107/T)$ s^{-1}
** 15.	$O(^1D_2) + H_2O \rightarrow 2OH$	3.0×10^3
16.	$OH + OH \rightarrow H_2O + O$	$2.46 \times 10^2 \exp(-550/T)$
17.	$OH + OH + M \rightarrow H_2O_2 + M$	$7.56 \exp(900/T)$
18.	$H_2O_2 + h\nu \rightarrow 2OH$	3.6×10^{-6} s^{-1} [b]
19.	$OH + H_2O_2 \rightarrow H_2O + HO_2$	$72.8 \exp(-164/T)$
20.	$OH + O_3 \rightarrow O_2 + HO_2$	$44.8 \exp(-930/T)$
* 21.	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	62
22.	$HO_2 + O_3 \rightarrow 2O_2 + OH$	$0.344 \exp(-580/T)$
23.	$HO_2 + OH \rightarrow H_2O + O_2$	7.4×10^2
24.	$NO + OH + M \rightarrow HNO_2 + M$	3.0×10^2
25.	$NO + HO_2 \rightarrow NO_2 + OH$	$81.2 \exp(254/T)$
26.	$NO_2 + OH + M \rightarrow HNO_3 + M$	$2.31 \times 10^{13} \exp((-26.6\ T/(17.4 + T)) - 0.5 \ln(T/280))$

Table 6 (Cont.)

	Reaction	Rate Constant[a]
27.	$NO_2 + HO_2 + M \rightarrow HO_2NO_2 + M$	25
28.	$HO_2NO_2 + M \rightarrow NO_2 + HO_2 + M$	$1.4 \times 10^{14} \exp(-10420/T)\ s^{-1}$
29.	$HNO_2 + h\nu \rightarrow NO + OH$	$2.8 \times 10^{-3}\ s^{-1}$ [b]
30.	$HNO_3 + h\nu \rightarrow NO_2 + OH$	$5.6 \times 10^{-7}\ s^{-1}$ [b]
31.	$HNO_2 + OH \rightarrow H_2O + NO_2$	1.4×10^2
32.	$HNO_3 + OH \rightarrow H_2O + NO_3$	2.0
33.	$NO_3 + NO_2 \rightarrow NO + O_2 + NO_2$	$5.59 \exp(-1000/T)$
34.	$NO_3 + NO_2 + M \rightarrow N_2O_5 + M$	$3.64 \exp(861/T)$
35.	$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$	$1.24 \times 10^{14} \exp(-10317/T)\ s^{-1}$
36.	$N_2O_5 + H_2O \rightarrow 2HNO_3$	3.2×10^{-7}
37.	$SO_2 + h\nu \rightarrow SO_2(^3B_1)$	$1.7 \times 10^{-5}\ s^{-1}$ [b]
38.	$SO_2(^3B_1) + M \rightarrow SO_2 + M$	$2.0 \times 10^6\ s^{-1}$
39.	$SO_2(^3B_1) + O_2 \rightarrow SO_3 + O$	0.07
N. 40.	$O + SO_2 + M \rightarrow SO_3 + M$	$20.6 \exp(-1120/T)$
41.	$SO_3 + H_2O \rightarrow H_2SO_4$	22
42.	$SO_2 + OH + M \rightarrow HSO_3 + M$	30
43.	$SO_2 + HO_2 \rightarrow SO_3 + OH$	2.2×10^{-2}
44.	$SO_2 + NO_3 \rightarrow SO_3 + NO_2$	0.25
N. 45[c].	$RCH{=}CH_2 + O + xNO \xrightarrow{O_2} RCHO + HCHO + xNO_2 + yO_3$	$1.01 \times 10^2 \exp(-38/T)$ [d]
46[c].	$RCH{=}CH_2 + O_3 + xNO \xrightarrow{O_2} RCHO + HCHO + xNO_2 + yO_3$	$0.15 \exp(-1900/T)$ [d]
** 47.	$RCH{=}CH_2 + OH \xrightarrow{O_2} R'O_2 + H_2O$	1.9×10^2 [d]
** 48.	$RCH{=}CH_2 + OH \xrightarrow{O_2} R'CHO + HO_2$	1.2×10^2 [d]

Table 6 (Cont.)

		Reaction	Rate Constant[a]
**	49.	$RCHO + h\nu \xrightarrow{2O_2} RO_2 + CO + HO_2$	8.6×10^{-5} s^{-1} [b,d]
**	50.	$OH + CO \xrightarrow{O_2} CO_2 + HO_2$	7.4
N.	51.	$RCHO + O \xrightarrow{O_2} RCO_3 + OH$	13[d]
**	52.	$RCHO + OH \xrightarrow{O_2} RCO_3 + H_2O$	3.9×10^2 [d]
**	53.	$RCO_3 + NO_2 + M \rightarrow PAN + M$	1.2×10^2 [d]
**	54.	$RCO_3 + NO \xrightarrow{O_2} RO_2 + CO_2 + NO_2$	2.1×10^2 [d]
	55.	$RCO_3 + SO_2 \xrightarrow{O_2} RO_2 + CO_2 + SO_3$	7.0×10^{-3} [d]
	56.	$HCHO + h\nu \rightarrow CO + H_2$	9.9×10^{-5} s^{-1} [b]
**	57.	$HCHO + h\nu \xrightarrow{2O_2} 2HO_2 + CO$	2.7×10^{-5} s^{-1} [b]
	58.	$H_2 + OH \xrightarrow{O_2} HO_2 + H_2O$	$8.86 \times 10^2 \exp(-2590/T)$
N.	59.	$HCHO + O \xrightarrow{O_2} HO_2 + CO + OH$	$4.92 \times 10^2 \exp(-1450/T)$
**	60.	$HCHO + OH \xrightarrow{O_2} H_2O + HO_2 + CO$	2.6×10^2
	61.	$RO_2 + NO \xrightarrow{O_2} R'CHO + HO_2 + NO_2$	88[e]
	62.	$RO_2 + HO_2 \rightarrow ROOH + O_2$	$1.89 \exp(1296/T)$ [e]
	63.	$2RO_2 \xrightarrow{O_2} 2R'CHO + 2HO_2$	3.9[e]
	64.	$RO_2 + SO_2 \xrightarrow{O_2} SO_3 + RCHO + HO_2$	6.0×10^{-2} [e]
	65.	$RH + OH \xrightarrow{O_2} RO_2 + H_2O$	50[f]
	66.	$HCl + OH \rightarrow H_2O + Cl$	$73.8 \exp(-425/T)$
	67.	$Cl + RH \xrightarrow{O_2} HCl + RO_2$	$1.79 \times 10^3 \exp(-61/T)$ [e]

Table 6 (Cont.)

	Reaction	Rate Constant[a]
68.	$Cl + RCH{=}CH_2 \xrightarrow{O_2} HCl + RO_2$	7.3×10^{2} [d]
69.	$Cl + HCHO \xrightarrow{O_2} HCl + CO + HO_2$	1.9×10^{3}
70.	$Cl + RCHO \xrightarrow{O_2} HCl + RCO_3$	1.9×10^{3} [d]
71.	$Cl + H_2 \xrightarrow{O_2} HCl + HO_2$	$8.61 \times 10^{2} \exp(-2290/T)$
72.	$OH + H_2S \xrightarrow{2O_2} H_2O + SO_2 + O + OH$	1.3×10^{2}
73.	$Cl + H_2S \xrightarrow{2O_2} HCl + SO_2 + O + OH$	1.5×10^{3}
N. 74.	$OH + OCS \xrightarrow{2O_2} SO_2 + CO_2 + O + OH$	1.4
N. 75.	$OH + CS_2 \xrightarrow{2O_2} SO_2 + OCS + O + OH$	4.6
N. 76.	$O + CS_2 \xrightarrow{3O_2} 2SO_2 + 2O + CO$	$1.48 \times 10^{3} \exp(-845/T)$
77.	$OH + CH_4 \xrightarrow{O_2} CH_3O_2 + H_2O$	0.16
78.	$Cl + CH_4 \xrightarrow{O_2} CH_3O_2 + HCl$	$2.45 \times 10^{2} \exp(-1370/T)$
79.	$CH_3O_2 + RO_2 \rightarrow R'OH + HCHO + CH_3OH + RCHO + O_2$	7.5[e]
N. 80.	$ROH + OH \xrightarrow{O_2} H_2O + R'CHO + HO_2$	64[e]
81.	$ROOH + h\nu \xrightarrow{O_2} R'CHO + HO_2 + OH$	1.2×10^{-5} s^{-1} [b,e]
82.	$ROOH + OH \rightarrow H_2 + RO_2$	21[e]
83.	$CH_3O_2 + SO_2 \xrightarrow{O_2} SO_3 + HCHO + HO_2$	0.12
** 84.	$CH_3O_2 + NO \xrightarrow{O_2} NO_2 + HCHO + HO_2$	1.7×10^{2}
85.	$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$	$1.89 \exp(1296/T)$

Table 6 (Cont.)

	Reaction	Rate Constant[a]
86.	$2CH_3O_2 \xrightarrow{O_2} 2HCHO + 2HO_2$	3.9
87.	$2CH_3O_2 \rightarrow CH_3OH + HCHO + O_2$	7.5
88.	$CH_3O_2 + RO_2 \xrightarrow{O_2} R'CHO + HCHO + 2HO_2$	3.9[e]
N. 89.	$CH_3OH + OH \xrightarrow{O_2} HCHO + H_2O + HO_2$	25
90.	$CH_3OOH + h\nu \xrightarrow{O_2} HCHO + HO_2 + OH$	1.2×10^{-5} s^{-1}[b]
91.	$PAN + M \xrightarrow{O_2} RO_2 + CO_2 + NO_3 + M$	3.0×10^{-3} s^{-1}[d]
92.	$CH_3OOH + OH \rightarrow CH_3O_2 + H_2O$	21
93.	$2RO_2 \rightarrow ROH + R'CHO + O_2$	7.5[e]

a All rate constants are quoted in units of ppm^{-1} s^{-1} unless otherwise stated and are applicable over the temperature range, T = 278-298 K. For reactions involving a third body the value quoted is for the product k[M] where [M] is 1 atmosphere of air.

b Rate constant is dependent on solar photon flux. The value listed is a maximum and is modified in the model to take account of latitude, time of day and day in the year.

c x = 0.953 and y = 0.047

d Value quoted is for R = CH_3

e Value quoted is for R = CH_3CH_2

f Value quoted is for R = $CH_3CH_2CH_2$