

Implementation of a chemistry module into the ECMWF Integrated Forecast System

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Deliverable
G-RG WP 4.4

Abstract

A description and initial evaluation of the tropospheric chemistry scheme as implemented into ECMWF's Integrated Forecast System (IFS) is presented, which is referred to as C-IFS. This includes a description of the photochemical mechanism, the interaction with aerosol, and the treatment of the stratosphere. These modules are mostly based on the parameterization in the global chemistry transport model TM5 and includes a recently updated chemical mechanism, selected from the CBM4 and CB05 schemes. We show a first evaluation of chemical budgets as compared to the offline version of the model, version TM5-chem-v3.2. The current version of C-IFS exhibits a relatively large oxidative capacity at a global scale. The methane lifetime is 7.7 yr, which is ~ 10% lower than the offline model version. Therefore the CO burden is also ~10% lower in C-IFS. This points at an excess of NO_x in the free troposphere, which needs further investigation.

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1. Introduction

A major new development in the MACC G-RG subproject concerns the development of inline chemistry within IFS, which is referred to as C-IFS. The C-IFS system could resolve limitations of the current coupled CTM-IFS system, for instance tracer concentration displacement issues between the CTM and IFS, and improve the computational efficiency.

Building blocks of the C-IFS system are the chemistry and photolysis module, as well as modules for emission, dry and wet deposition (see deliverables 4.5 and 4.6). In this report we will describe the photo-chemistry module, which is based on the TM5-chem-v3.0 scheme (Huijnen et al., 2010), updated according to the recent developments in order to include more explicit chemistry from higher hydrocarbons (TM5-chem-v3.2). In subsequent sections we provide information on the chemistry and the photolysis scheme. Also we show a first evaluation of the chemical budgets as compared to the offline model version, in order to present the current state of the system, and address aspects that require further investigation.

2. Tropospheric chemistry

The chemical mechanism is based on an updated version of the modified Carbon Bond Mechanism 4 (CBM4) scheme originally described in Houweling et al. (1998), which is based on the CBM4 mechanism of Gery et al. (1989). The CBM4 scheme adopts a lumping approach for organic trace gas species by defining a separate tracer species for specific types of functional groups (e.g. ALD2 represents higher aldehydes). The speciation of the explicit organic compounds that are introduced in terms of lumped species follows the recommendations given in Yarwood et al. (2005). Recently this scheme has been extended to include explicit chemistry for CH₃OH, C₂H₆, C₃H₈, C₃H₆ as well as an updated isoprene chemistry scheme (Yarwood et al., 2005), and a modified NO_x recycling scheme (Zaveri and Peters, JGR 1999).

The scheme is supplemented with chemical reactions for the oxidation of sulphur dioxide (SO₂), di-methyl sulphide (DMS), methyl sulphonic acid (MSA) and ammonia (NH₃). For the oxidation of DMS, the approach of Chin et al. (1996) is adopted. Table 1 gives a comprehensive list of the trace gases included in the chemical scheme. In total there are 53 chemical species, including the radioactive tracers radon (²²²Rn) and lead (²¹⁰Pb), a stratospheric ozone tracer, and a polar stratospheric clouds (PSC) tracer. The nitrogen oxide species NO and NO₂, the nitrate radical (NO₃), N₂O₅ and HNO₄ are transported as a lumped aggregate. A separate tracer is used for transporting sulphate aerosol (SO₄²⁻).

The reaction rates have been updated according to the latest recommendations given in either Sander et al. (2006) or Atkinson et al. (2004; 2006). The oxidation of CO by OH implicitly accounts for the formation and subsequent decomposition of the intermediate species HOCO as outlined in Sander et al. (2006). For lumped species such as ALD2, the reaction rate is determined using an average of the rates of reaction for the C2 and C3 aldehydes, which are considered to be the most abundant. A comprehensive list of all reaction rates and the associated reaction data employed is provided in Appendix 1.

For the loss of gaseous trace species via heterogeneous oxidation processes, the model explicitly accounts for the oxidation of SO₂ in cloud through aqueous phase reactions with H₂O₂ and O₃, depending on the acidity of the solution.

Table 1. The chemical trace species which are included in the tropospheric chemistry version of TM5. The definitions of the lumped species, aerosols and operators are: [1] paraffinic carbon atoms, [2] olefinic carbon bonds, [3] CH₃CHO and higher aldehydes, [4] higher organic peroxides, [5] alkyl nitrates, [6] sulphate aerosol, [7] organic ethers, [8] PAR budget corrector, [9] NO to NO₂ operator, [10] NO to alkyl nitrate operator and [11] ammonium aerosol. The O(¹D) species is not specifically included in the scheme.

Chemical Trace Species	(continued)	(continued)
O ₃	PAR ^[1]	NO
NO _x	C ₂ H ₄	NO ₂
H ₂ O ₂	OLE ^[2]	NO ₃
CH ₄	ALD2 ^[3]	N ₂ O ₅
CO	PAN	HNO ₄
HNO ₃	ROOH ^[4]	CH ₃ COCHO
CH ₃ OOH	ORGNTR ^[5]	C ₂ O ₃
CH ₂ O	SO ₂	ROR ^[7]
CH ₃ OH	DMS	RXPAR ^[8]
HCOOH	MSA	XO ₂ ^[9]
MCOOH	SO ₄ ²⁻ ^[6]	XO ₂ N ^[10]
C ₂ H ₆	PSC	ETHP
ETHOOH	222Rn	NAP
ETHOH	210Pb	ISPD
C ₃ H ₈	OH	NH ₂
C ₃ H ₆	HO ₂	NH ₃
ISOP	CH ₃ O ₂	NH ₄ ⁺ ^[11]
TERP		

3. Photolysis

For the calculation of photodissociation rates an offline parameterization for the derivation of actinic fluxes is used which is based on the work of Landgraf and Crutzen (1998) and expanded according to Krol and van Weele (1997) to account for the variations in actinic fluxes below, in and above clouds, variations caused by snow and ice surfaces with high albedo, and variations in the (largely stratospheric) overhead O₃ column. The approach uses 7 absorption bands across the spectral range 202 – 752.5 nm as defined in Landgraf and Crutzen (1998).

The pre-calculated actinic fluxes are indexed using the relevant temperature, pressure and optical depth at a particular model level when accounting for clouds, ozone and surface albedo following Krol and van Weele (1997). Although heavily parameterized, this method avoids the radiative transfer calculation of the actinic flux for each of the 140 spectral bins included on the wavelength grid. The optical depth of clouds is calculated based on a

parameterization available in IFS for the cloud optical thickness at 550 nm. In total 17 photolysis rates are included in the scheme, see Table 2.

Table 2. The photolysis reactions included in the model. Only shown are the reaction products that are calculated explicitly by the chemical solver. The quantum yield for the production of O(¹D) from the photolysis of O₃ is taken from Shetter et al. (1996).

Stoichiometry	
O ₃ + <i>hν</i> →	O(¹ D)
NO ₂ + <i>hν</i> →	NO + O ₃
H ₂ O ₂ + <i>hν</i> →	2OH
HNO ₃ + <i>hν</i> →	OH + NO ₂
HNO ₄ + <i>hν</i> →	HO ₂ + NO ₂
N ₂ O ₅ + <i>hν</i> →	NO ₂ + NO ₃
CH ₂ O + <i>hν</i> →	CO
CH ₂ O + <i>hν</i> →	CO + 2HO ₂
CH ₃ OOH + <i>hν</i> →	CH ₂ O + HO ₂ + OH
NO ₃ + <i>hν</i> →	NO ₂ + O ₃
NO ₃ + <i>hν</i> →	NO
PAN + <i>hν</i> →	C ₂ O ₃ + NO ₂
ORGNTR + <i>hν</i> →	NO ₂ + 0.41 XO ₂ + 0.1 ETHP + 0.3ALD2 + 0.9 HO ₂ + 0.74 C ₂ O ₃ + 0.74 CH ₃ O ₂ + 1.98RXP
ALD2 + <i>hν</i> →	CH ₂ O + XO ₂ + CO + 2HO ₂
CH ₃ C(O)CHO + <i>hν</i> →	C ₂ O ₃ + HO ₂ + CO
ROOH + <i>hν</i> →	OH+0.4 XO ₂ +0.74C ₂ O ₃ +0.74 CH ₃ O ₂ +0.3 ALD2+0.1 ETHP + 0.9HO ₂ +1.98 RXP
ISPD + <i>hν</i> →	0.333CO + 0.067 ALD2 + 0.9 CH ₂ O + 8.832 PAR + 1.033 HO ₂ + 0.7 XO ₂ + 0.967 C ₂ O ₃

4. The chemical solver

The chemical solver used in C-IFS is the same as for TM5, which is the Euler Backward Iterative (EBI) solver (Hertel et al., 1996). This solver has been specifically designed for use with the CBM4 mechanism of Gery et al. (1989). The chemical time step employed is typically 15 minutes. Different from the offline model, the emission of NO and dry deposition terms are standard not included during the solution of the differential equations, but applied elsewhere. In order to achieve a converged solution of the differential equations the number of iterations for each chemical species varies depending on the atmospheric lifetime of each particular species and is larger in the boundary layer, where the perturbations due to emissions can be large. For some circumstances, where fast chemical processes dominate (i.e. in high NO_x environments), a mass balance step is applied to the gas phase components of NO_y, where NO_y is defined as the sum of NO, NO₂, NO₃, HNO₃, HNO₄, 2×N₂O₅, PAN and ORGNTR, to ensure no artificial loss of nitrogen occurs.

5. Stratospheric boundary conditions

The modified CBM4 chemical mechanism does not include either halogenated species or photolytic destruction below 202 nm, and is therefore not adequate for the description of stratospheric chemical processes. Thus realistic upper boundary conditions for the longer-lived gases such as O₃, CH₄, and HNO₃ must be provided in order to capture the influence of stratospheric intrusions on the composition of the upper troposphere. The stratospheric O₃ concentrations are described by the Cariolle scheme (Cariolle and Teysedre, 2007). Chemical tendencies for stratospheric and tropospheric O₃ are merged at an empirical interface of the functionality $P = 230 - 148 \cos(\text{lat})^4$ [hPa], which approximately describes the zonal average pressure level at which ozone concentrations exceed 150 ppbv. It should be noted that the magnitude of stratosphere-troposphere exchange depends on the strength of the overturning circulation, which has been shown to be different for the different ECMWF reanalyses (e.g. ERA-40, ERA-Interim) and operational data sets (e.g. Van Noije et al., 2004; 2006; Monge-Sanz et al., 2007). This affects the tropospheric O₃ budget and chemistry of the upper troposphere significantly.

For HNO₃ a stratospheric climatology based on the UARS MLS satellite observations is applied by prescribing the ratio of HNO₃/O₃ at 10 hPa. Different to the offline model version methane in the stratosphere are not yet nudged to a climatology. Such a constraint could implicitly account for the stratospheric chemical loss of CH₄ by OH, Cl and O(¹D).

6. Evaluation of chemical budgets

An evaluation of the various tropospheric chemistry budgets is performed, as compared against the offline TM5 model. In the current implementation of C-IFS total and tropospheric budgets due to loss by OH and photolysis are stored. Additionally budget terms to close O₃ production and loss are retained, but other chemical budget terms remain unknown in C-IFS. However, together with budgets for emissions, dry and wet deposition, a relatively complete picture of the chemistry scheme and its essential differences compared to the offline version can be constructed. Here we evaluate a simulation for the year 2007, using emissions that have been prescribed for the POLMIP model intercomparison project. Both versions start from the same initial conditions.

The tropospheric OH production budget is given in Table 3. The primary OH production from O₃ photolysis is 7% higher in C-IFS compared to TM5. Additionally the radical recycling terms (NO + HO₂ and O₃ + HO₂) are 23% higher, leading to a significantly higher OH production in C-IFS compared to TM5. This explains the larger CH₄ loss in C-IFS, table 4. The CH₄ lifetime is accordingly only 7.7 year in C-IFS, compared to 8.5 year in TM5.

As methane surface concentrations are fixed by a zonally varying field, the CH₄ emissions to compensate for the OH loss are larger in C-IFS compared to TM5. The larger CH₄ oxidation explains the increase in chemical production of CO in the troposphere via CH₂O photolysis and oxidation, table 5. Still the CO burden is lower by 10%, as the oxidation term is more negative than the increase in the tropospheric CO production.

The C-IFS model exhibits significantly larger O₃ production and loss compared to the offline model, table 6. Although the total budget of O₃ photolysis is larger we assured that the global annual photolysis rates in the boundary layer are very similar, indicating that the photolysis scheme including estimates of the total overhead column as derived from the Cariolle chemistry scheme, are likely not the cause of these differences. More probably the increased O₃ production as well the as the stronger OH recycling is explained by an excess of NO_x in the free troposphere. An evaluation against tropospheric SCIAMACHY NO₂ observations (not shown here) also indicated relatively large NO₂ background values, which were much larger compared to the offline model version. The reasons for this excess in NO_x is not yet understood. It still could point at a problem in the photolysis scheme, leading to erroneous chemical equilibrium of NO/NO₂, and/or other compounds of the NO_y family. Another explanation could be spurious transport effects, such as an excess of transport of stratospheric NO_x into the troposphere, or an over-estimation of NO_x exchange between the boundary layer and free troposphere, where its lifetime can be much longer. These aspects require further investigation.

Table 3. annual OH production (Tg OH). Dashes in C-IFS budgets indicate unknown magnitudes.

	C-IFS	TM5
Trop. Chem. Prod.		
- O(¹ D) + H ₂ O	1771	1657
- NO + HO ₂	1250	991
- O ₃ + HO ₂	503	427
- Remaining	-	429

Table 4. annual CH₄ budget (Tg CH₄). CH₄ lifetime is calculated as (Burden / (Trop loss + 70 Tg), Prather et al., 2001)

	C-IFS	TM5
Emis	566	520
Trop. Chem. loss	554	496
Burden (Tg CH ₄)	4817	4839
Lifetime (yr)	7.7	8.5

Table 5. annual CO budget (Tg CO). Dashes in C-IFS budgets indicate unknown magnitudes.

	C-IFS	TM5
Emis	1050	1060
Trop. Chem. Prod:		
- CH ₂ O + hv	1018	948
- CH ₂ O + OH	396	311
- Remaining terms	-	143
Trop. Chem. Loss (OH)	2414	2240
Dry dep	179	182
Wet dep	13	0
Burden (Tg CO)	315	349

Table 6. annual O₃ budget (Tg O₃). Dashes in C-IFS budgets indicate unknown magnitudes.

	C-IFS	TM5
Trop. Chem. Prod.	5234	4406
Trop. Chem. Loss		
- O ₃ + hv	2501	2338
- O ₃ + OH	703	509
- O ₃ + HO ₂	1422	1206
- Remaining terms	-	102
Dry dep	801	803
Glb Burden (Tg O ₃)	3172	3098

7. Integration in the IFS code

The routine of the CBM4 chemistry (chem_tm5) is called from the chemistry interface (chem_main). Its output are tendencies of the tracer mass mixing ratios. The chemistry interface is call from the IFS routine for physical parameterisations (callpar).

The mass mixing ratios at the beginning of the time step are used for the calculation of the chemical tendencies. The tendencies of the chemical conversion are added to the tendencies describing emission injection, advection, diffusion, dry and wet deposition.

Table 7 list the routines added to the IFS code. The chemistry routine is implemented in research perforce branches of the cycles 35R1, 35R3, 36R1 and 36R3.

Table 7. Routines added to the IFS code

Routine name	Called from	Purpose	Output
chem_tm5.F90	chem_main	CBM4 chemistry	Chemical tendencies
chem_mix.F90	All	Module	-
tm5_chem_module.F90	All	Tm5 chemistry module	-
tm5_chem_ini.F90	chem_init	Initialization of chemical rates and photolysis lookup table	-
O3chem (already part of IFS)	chem_tm5	Linear ozone chemistry	O3 tendencies
tm5_calrates	chem_tm5	Calculation of reaction rates	Reaction rates
tm5_photolysis_rates	chem_tm5	Calculation of photolysis rates	Photolysis rates
tm5_fparam	tm5_photolysis_rates	Calculation of actinic fluxes	Actinic fluxes
tm5_getextra	chem_tm5	Preparation of data arrays required for EBI solver	Input arrays for EBI solver
tm5_do_ebi	chem_tm5	Actual Euler Backward Integrator	Updated concentration fields due to photochemistry
tm5_noy	chem_tm5	Ensure NO _y mass conservation	Updated NO _y concentration fields
tm5_budg	chem_tm5	Calculate budgets of photochemical rates	photochemical budgets
tm5_boundary_ch4	chem_tm5	Apply CH ₄ surface boundary conditions	Updated CH ₄ surface concentrations
tm5_boundary_hno3	chem_tm5	Apply HNO ₃ stratospheric boundary conditions	Updated HNO ₃ concentration fields at 10hPa

8. Conclusions

We have presented a first implementation of a chemical mechanism into ECMWF's Integrated Forecast System, based on the TM5 chemistry transport model. This scheme consists of 54 tracers and 95 reactions, and is based on the CBM4 mechanism, extended with explicit C2 and C3 chemistry, and selected updates based on CB05. The 17 photolysis rates are calculated based on a lookup table with pre-calculated actinic fluxes. Stratospheric O₃ concentrations are constrained by the Cariolle scheme. A first evaluation of chemical budgets indicates a relatively high oxidative capacity, with a methane lifetime of 7.7 year, which is ~10% lower than the offline model version using the same chemistry and emissions. A further analysis of the budgets indicates an excess of NO_x in the free troposphere, which requires further investigation.

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Appendix 1: the chemical mechanism

Table A1. The gas-phase chemical mechanism applied in the tropospheric chemistry version of TM5. The reaction products O₂ and H₂O are not shown. The reactions involving SO₂, DMS and NH₃ have been added onto the modified CBM4 scheme of Houweling et al. (1998) in order to account for the oxidation of the respective species. All reactions of the NH₂ radical act as sink processes for the respective radicals and oxidants. The source of the rate data is as follows: [1] Sander et al. (2006), [2] Yarwood et al. (2005), [3] Atkinson et al. (2006), [4] Gery et al. (1989), [5] Houweling et al. (1998), [6] Atkinson et al. (2004), [7] Zaveri and Peters (1999), [8] taken from MOZART chemical scheme, [9] CH₂O and PAR yield increased, M. Karl, pers. comm. (2010).

Reactants	Products	Rate Expression	Reference
NO + O ₃	NO ₂	3.0E-12*exp(-1500/T)	[1]
NO + HO ₂	NO ₂ + OH	3.5E-12*exp(250/T)	[1]
NO + CH ₃ O ₂	CH ₂ O + HO ₂ + NO ₂	2.8E-12*exp(300/T)	[1]
NO ₂ + OH (+ M)	HNO ₃	K ₀ = 1.8E-30*(300/T) ^{3.0} K _∞ = 2.8E-11	[1]
OH + HNO ₃	NO ₃	K ₀ = 2.41E-14*(460/T) K ₂ = 6.51E-34*(1335/T) K ₃ = 2.69E-17*(2199/T)	[1]
NO ₂ + O ₃	NO ₃	1.2E-13*exp(-2540/T)	[1]
NO + NO ₃	NO ₂ + NO ₂	1.5E-11*exp(170/T)	[1]
NO ₂ + NO ₃	N ₂ O ₅	K ₀ = 2.0E-30*(300/T) ^{4.4} K _∞ = 1.4E-12*(300/T) ^{0.7}	[1]
N ₂ O ₅	NO ₂ + NO ₃	2.7E-27*exp(11000/T)	[1]
OH + HNO ₄	NO ₂	1.3E-12*exp(380/T)	[1]
NO ₂ + HO ₂	HNO ₄	K ₀ = 2.0E-31*(300/T) ^{3.4} K _∞ = 2.9E-12*(300/T) ^{1.1}	[1]
HNO ₄ (+ M)	NO ₂ + HO ₂	2.1E-27*exp(10900/T)	[1]
O(¹ D) (+ M)		3.3E-11*exp(55/T)*[O ₂] + 2.15E11*exp(110/T)*[N ₂]	[1]
O(¹ D) + H ₂ O	OH + OH	1.63E-10*exp(60/T)	[1]

O ₃ + HO ₂	OH	1.0E-14*exp(-490/T)	[1]
CO + OH	HO ₂	K ₀ = 5.9E-33*(300/T) ^{1.4}	[1]
		K _∞ = 1.1E-12*(300/T) ^{-1.3}	
		K ₀ = 1.5E-13*(300/T) ^{-0.6}	
		K _∞ = 2.1E9*(300/T) ^{-6.1}	
O ₃ + OH	HO ₂	1.7E-12*exp(-940/T)	[1]
OH + H ₂ O ₂	HO ₂	1.8E-12	[1]
OH + CH ₂ O	CO + HO ₂	5.5E-12*exp(125/T)	[1]
OH + CH ₄	CH ₃ O ₂	2.45E-12*exp(-1775/T)	[1]
OH + CH ₃ OOH	0.7 CH ₃ O ₂ + 0.3 CH ₂ O + 0.3 OH	3.8E-12*exp(200/T)	[1]
OH + ROOH	0.77 XO ₂ + 0.19 MGLY + 0.04 ALD2 + 0.23 OH + RXPAR	3.01E-12*exp(190/T)	[7]
CH ₃ O ₂ + HO ₂	CH ₃ OOH	4.1E-13*exp(750/T)	[1]
CH ₃ O ₂ + CH ₃ O ₂	0.66 CH ₂ O + 0.32 HO ₂ + 0.34 CH ₃ OH	9.5E-14*exp(390/T)	[7]
OH + HO ₂		4.8E-11*exp(250/T)	[1]
HO ₂ + HO ₂	H ₂ O ₂	3.5E-13*exp(430/T)	[1]
		1.77E-33*exp(1000/T)	
		1.4E-21*exp(2200/T)	
OH + H ₂	HO ₂	2.8E-12*exp(-1800/T)	[1]
NO ₃ + CH ₂ O	HNO ₃ + CO + HO ₂	5.8E-16	[1]
ALD2 + OH	C ₂ O ₃	Average of : 4.4E-12*exp(365/T)	[3]
		5.1E-12*exp(405/T)	[3]
ALD2 + NO ₃	C ₂ O ₃ + HNO ₃	Average of : 1.4E-12*exp(-1860/T)	[3]
		6.5E-15	[3]
NO + C ₂ O ₃	CH ₃ O ₂ + NO ₂	8.1E-12*exp(270/T)	[1]
NO ₂ + C ₂ O ₃	PAN	K ₀ = 2.7E-28*(300/T) ^{7.1}	[3]
		K _∞ = 1.2E-11*(300/T) ^{0.9}	
PAN	NO ₂ + C ₂ O ₃	K ₀ = 4.9E-3*exp(-12100/T)	[3]
		K _∞ = 5.4E16*exp(-13830/T)	
NO ₃ + HO ₂	HNO ₃	4.0e-12	[7]
NO ₃ + CH ₃ O ₂	NO ₂ + HO ₂ + HCHO	1.2e-12	[7]
NO ₃ + C ₂ O ₃	NO ₂ + CH ₃ O ₂	4.0e-12	[7]
NO ₃ + XO ₂	NO ₂	2.5e-12	[7]
NAP + NO	1.5NO ₂ + 0.5HCHO + 0.5ALD2 + 0.5ORGNTR + 0.5HO2 + RXPAR	4.0e-12	[7]
NAP + HO ₂	ORGNTR	1.7e-13*exp(1300./T)	[7]
NAP + NO ₃	1.5NO ₂ + 0.5HCHO + 0.5ALD2 + 0.5ORGNTR + 0.5HO2 + RXPAR	2.5e-12	[7]
OH + CH ₃ OH	HCHO + HO ₂	2.85e-12*exp(-345/T)	[2]
OH + HCOOH	HO ₂	4.0e-13	[2]
OH + C ₂ H ₆	ETHP	6.9e-12*exp(-1000/T)	[7]
ETHP + NO	NO ₂ + HO ₂ + ALD2	2.55e-12*exp(380/T)	[7]
ETHP + NO ₃	NO ₂ + HO ₂ + ALD2	2.3e-12	[7]
ETHP + HO ₂	ETHOOH	4.3e-13*exp(870/T)	[7]
ETHP + ETHP	0.8ALD2 + 0.6HO ₂ + 0.2 C ₂ H ₆	6.4e-14	[7]
OH + ETHOOH	0.7ETHP + 0.3ALD2 + 0.3OH	6.0e-12	[7]
OH + C ₂ H ₅ OH	ALD2 + HO ₂ + 0.1 XO ₂ + 0.1HCHO	3.0e-12*exp(20/T)	[2]
OH + CH ₃ COOH	CH ₃ O ₂	4.2e-14*exp(-855/T)	[2]
OH + C ₃ H ₈	XO ₂	7.6e-12*exp(-585/T)	added

OH + C ₃ H ₆	XO ₂	ko = 8.0e-27 3-5 k _∞ = 3.0e-11	added
O ₃ + C ₃ H ₆	0.54HCHO + 0.19HO ₂ + 0.33OH + 0.56CO + 0.5ALD2 + 0.31CH ₃ O ₂ + 0.25HCOOH	5.5e-15*exp(-1880/T)	[8]
NO ₃ + C ₃ H ₆	ORGNTR	4.6e-13*exp(-1155/T)	added
C ₂ O ₃ + C ₂ O ₃	2 CH ₃ O ₂	2.9E-12*exp(500/T)	[1]
C ₂ O ₃ + HO ₂	0.4 CH ₃ COOH + 0.4 O ₃	4.3E-13*exp(1040/T)	[7]
OH + PAR	0.87 XO ₂ + 0.76 ROR + 0.11 HO ₂ + 0.11 ALD2 + 0.11 RXPAR + 0.13 XO ₂ N	8.1E-13	[4]
ROR	1.1 ALD2 + 0.96 XO ₂ + 0.04 XO ₂ N + 0.02 ROR + 2.1 RXPAR + 0.94 HO ₂	1E15*exp(-8000/T)	[4]
ROR	HO ₂	1600.0 (*)	[4]
OH + OLE	0.8 CH ₂ O + 0.95 ALD2 + 0.8 XO ₂ + 1.57HO ₂ + 0.7 RXPAR + 0.62 CO	Average of : 1.86E-11*exp(175/T) 8.12E-12*exp(610/T) 2.6E-12*exp(610/T)	[3] [3] [3]
O ₃ + OLE	0.5 ALD2 + 0.74 CH ₂ O + 0.76 HO ₂ + 0.22 XO ₂ + 0.95 CO + RXPAR + 0.1 OH	Average of : 8.5E-16*exp(-1520/T) 1.4E-15*exp(-2100/T) 1.0 E-17	[7] [7] [7]
NO ₃ + OLE	0.91 XO ₂ + CH ₂ O + 0.09 XO ₂ N + NO ₂ + 0.91 ALD2 + RXPAR + 0.56 HO ₂ + 0.56 CO	Average of : 4.0E-14*exp(-400/T) 6.0E-16 3.5E-15	[3] [3] [3]
OH + C ₂ H ₄ (+M)	HO ₂ + 1.56 CH ₂ O + 0.22 ALD2 + XO ₂	K ₀ = 1.0E-28*(300/T) ^{4.5} K _∞ = 8.8E-12*(300/T) ^{0.85}	
O ₃ + C ₂ H ₄	CH ₂ O + 0.22 HO ₂ + 0.12 OH + 0.24 CO + 0.52 HCOOH	1.2E-14*exp(-2630/T)	[7]
OH + CH ₃ COCHO	XO ₂ + C ₂ O ₃	1.5E-11	[3]
OH + TERP	1.22HO ₂ + 1.25XO ₂ + 0.25XO ₂ N + 1.22HCHO + 5.0PAR + 0.47ALD2 + 0.47CO	1.5e-11*exp(449/T)	[2,9]
O ₃ + TERP	0.57OH + 0.28HO ₂ + 0.76XO ₂ + 0.18XO ₂ N + 1.8HCHO + 0.211CO + 6.0PAR + 0.21ALD2 + 0.39C ₂ O ₃ + 0.39CH ₃ O ₂	1.2e-15*exp(-821/T)	[2,9]
NO ₃ + TERP	0.47NO ₂ + 0.75HO ₂ + 1.03XO ₂ + 0.25XO ₂ N + 0.47ALD2 + 0.53ORGNTR + 0.47CO + 6.0PAR	3.7e-12*exp(175/T)	[2,9]
OH + ISOP	0.912 ISPD + 0.991 XO ₂ + 0.629 CH ₂ O + 0.912 HO ₂ + 0.088 XO ₂ N	2.7E-11*exp(390/T)	[3]
O ₃ + ISOP	0.65 ISPD + 0.6 CH ₂ O + 0.066 CO + 0.2 C ₂ O ₃ + 0.15 ALD2 + 0.35 PAR + 0.066 HO ₂ + 0.2 XO ₂ + 0.266 OH	1.04E-14*exp(-1995/T)	[3]
NO ₃ + ISOP	0.65 ISPD + 0.8 HO ₂ + 0.8 ORGNTR + 0.8 ALD2 + 2.4 PAR + 0.2 NO ₂ + XO ₂	3.15E-12*exp(-450/T)	[3]
OH + ISPD	1.565PAR + 0.167HCHO + 0.503HO ₂ + 0.334CO + 0.168CH ₃ COCHO + 0.273ALD2 + 0.498C ₂ O ₃ + 0.713XO ₂	Average of: 1.86e-11*exp(175/T) 2.6e-12*exp(610/T)	[2]
O ₃ + ISPD	0.114C ₂ O ₃ + 0.15HCHO + 0.85 CH ₃ COCHO + 0.154HO ₂ + 0.268OH + 0.064XO ₂ + 0.02ALD2 +	Average of: 8.5e-16*exp(-1520/T) 1.4e-15*exp(-2100/T)	[2]

NO ₃ + ISPD	0.36PAR + 0.225CO 0.357ALD ₂ + 0.282HCHO + 1.282PAR + 0.925HO ₂ + 0.643CO + 0.85ORGNTR + 0.075C ₂ O ₃ + 0.075XO ₂ + 0.15HNO ₃	Average of: 6.0e-16 3.5e-15	[2]
NO + XO ₂	NO ₂	2.6E-12*exp(365/T)	[2]
XO ₂ + XO ₂		6.8E-14 ^[KC81]	[2]
			[3]
NO + XO ₂ N	ORGNTR	2.6E-12*exp(365/T) ^[KC79]	[2]
HO ₂ + XO ₂	ROOH	7.5E-13*exp(700/T) ^[KC82]	[2]
PAR + RXPAR		8E-11	[4]
OH + ORGNTR	NO ₂ + XO ₂	5.9E-13*exp(-360/T)	[7]
HO ₂ + XO ₂ N	ROOH	(KC81*KC82)/KC79	[5]
DMS + OH	SO ₂	1.1E-11*exp(-240/T)	[1]
DMS + OH	0.75 SO ₂ + 0.25 MSA	1.0E-39*exp(5820/T) 5.0E-30*exp(6280/T)	[1]
DMS + NO ₃	SO ₂	1.9E-13*exp(520/T)	[6]
OH + SO ₂	SO ₄ ²⁻	K ₀ = 3.3E-31*(300/T) ^{4.3} K _∞ = 1.6E-12*(300/T)	[1]
OH + NH ₃	NH ₂	1.7E-12*exp(-710/T)	[1]
NO + NH ₂		4.0E-12*exp(450/T)	[1]
NO ₂ + NH ₂		2.1E-12*exp(650/T)	[1]
HO ₂ + NH ₂		3.4E-11	[1]
O ₂ + NH ₂		6.0E-21	[1]
O ₃ + NH ₂		4.3E-12*exp(-930/T)	[1]