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February 6, 2003

Mr. Richard Corey
Chief, Research and Economics Branch
Research Division
California Air Resources Board
1001 I Street
P.O. Box 2518
Sacramento, California 95812

Re: Expanded List of Updated Maximum Incremental Reactivity (MIR) Values

Dear Mr. Corey:

You may remember that on October 26, 2002 I provided an updated list of Maximum Incremental Reactivity (MIR) values that your staff requested for the CARB's regulatory needs. These were calculated using the current version of my SAPRC-99 chemical mechanism, as described in my previous letter and also summarized below. Since that time, at the request of industry groups I added 9 new categories of VOCs for which I have calculated MIR values. I also was informed that the previous list had an incorrect molecular weight for diethyl benzene isomers, which resulted in the MIR's for those compounds being ~10% too high. I understand from Dongmin Luo of your staff that it is not too late to add new VOCs to your regulatory list, and that there is a desire from some industry groups that at least some of these new chemicals be included. Therefore, I am providing the CARB with an updated tabulation that includes these 9 new VOC categories and corrects the data for the diethylbenzenes. The previous list also had missing uncertainty assignments and upper limit MIR estimates for some of the added VOCs, and this has also been corrected.

An Excel file containing the updated reactivity tabulation is available at my reactivity web site at <http://www.cert.ucr.edu/~carter/reactdat.htm>, and is also being sent to you and Dr. Dongmin Lou of your staff as an email attachment. The summary page of the file, giving the updated MIR values, is attached.

The updates and additions made to the MIR tabulation relative to the values used in your current aerosol coatings rule is given below. Much of this is essentially the same as the discussion given in the letter of October 26, but is duplicated here for the convenience of those who may not have access to the October 26 letter.

Since neither the chemical mechanism nor the reactivity calculation scenarios or procedures have undergone any major revisions since the MIR values incorporated in the current aerosol coatings rule were calculated, one would not expect changes in MIRs for most of the species. However, some corrections have been made to some mechanism and emissions assignments for certain VOCs, and modifications or corrections have been made to some of the files and software programs. This has resulted in resulting in non-negligible MIR changes for a small number of VOCs and very small changes for many others. In particular, of the ~670 VOC categories on your list for which I have recalculated MIR values, the MIR's for 14 have changed by more than 10%, 26 have changed by more than 5%, and 305 have changed by more than 1%. In addition, in the process of making assignments for my mechanism for various emissions inventories, for other projects, and at the request of certain industry groups I have added 106 of new VOC categories for which MIRs have been calculated. Table 1, attached, lists the VOCs whose MIRs have changed by more than 5%, and Table 2 lists the new VOC categories that have been added to the current list. Footnotes to Table 1 indicate the reasons or probable reasons for the changes. (These tables are available in Word format at <ftp://ftp.cert.ucr.edu/pub/carter/SAPRC99/s99corr3.doc>.)

Note that Table 1 is exactly the same as the corresponding table in the October 26 letter, but that Table 2 includes the 9 new VOC categories as well as those given in the previous letter. In addition, the MIR's for some of the new species added on October 26 and listed on Table 2 have changed slightly in this update. This is because for this update their MIR's were calculated using the "adjusted product" method as described in Section III.M of the SAPRC-99 documentation report (Carter, 2000), while for the October 26 version they were calculated using the fixed product method. As described in the SAPRC-99 documentation, the adjusted product method provides a slightly more detailed estimated mechanism for deriving estimated mechanisms for MIR calculations that does not require significantly more calculation effort, so it was incorporated as part of this update. The model species list included with the reactivity tabulation provided electronically (or at by above-referenced reactivity web site) now includes a column indicating whether the adjusted product method was used when deriving the mechanism used in the MIR calculation.

The tabulation used in your current regulation includes MIRs for a number of species that were derived by CARB staff based on the upper limit estimation method. I did not review these estimates, but I presume that they were made using the appropriate procedures and parameters. No updates have been made to the recommended procedures that would affect these upper limit MIR estimates, so I do not recommend any changes being made to these upper limit estimates. In addition, as indicated on Table 1, a few VOC categories for which you have made upper limit estimates are included on the current tabulation with lower estimated MIR values. My estimates of the uncertainties for the reactivities of these compounds have not been reduced, so I recommend that you continue to use the upper limit estimates for those compounds for your regulatory scale.

Note that a few VOC categories on the tabulation, such as benzaldehyde, have negative estimated MIRs, while the table in your regulation uses zero for the MIR. Although this is a policy issue that is up to the CARB, I recommend you continue using zero values for the MIRs for these species in your regulations.

William P. L. Carter
Updated MIR Values

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I hope this is useful to the CARB. If you or your staff have any questions or issues about this new tabulation or any of the changes or new species that were added, please let me know.

Sincerely,

William P. L. Carter
Research Chemist

Cc: Dr Dongmin Luo
Atmospheric Processes Research Section

Table 1. Listing of VOC species or categories whose MIR values have changed by more than 5%.

Model Name	Description	MIR (gm O ₃ /gm VOC)			Note
		Updated	Previous	Change	
CL2IBUTE	2-(chloromethyl)-3-chloropropene	3.13	1.13	177%	[a]
AMP	2-Amino-2-Methyl-1-Propanol	4.75	15.08	-68%	[b]
TM-AMINE	Trimethyl Amine	7.06	16.60	-57%	[b]
244M2C5E	2,4,4-trimethyl-2-Pentene	8.52	5.85	46%	[c]
METHANE	Methane	0.014	0.01	39%	[d]
CYC-C15	C15 Cycloalkanes	0.65	0.99	-34%	[e]
PROPACID	Propionic Acid	0.79	1.16	-32%	[f]
ACETACID	Acetic Acid	0.50	0.71	-30%	[f]
2ETHXACD	2-Ethyl Hexanoic Acid	3.49	4.41	-21%	[f]
ME-BR	Methyl Bromide	0.017	0.02	-16%	[d]
CH3-CL	Methyl Chloride	0.034	0.03	15%	[d]
CHCL3	Chloroform	0.034	0.03	14%	[d]
ETOX	Ethylene Oxide	0.044	0.05	-11%	[d]
DPGOME2	Dipropylene Glycol Methyl Ether isomer (2-[2-methoxypropoxy]-1-propanol)	2.70	3.02	-11%	[g]
C7-OLE1	C7 Terminal Alkenes	4.20	4.56	-8%	[h]
1-HEPTEN	1-Heptene	4.20	4.56	-8%	[h]
11BR2-C2	1,2-Dibromoethane	0.046	0.05	-7%	[d]
C15-OLE1	C15 Terminal Alkenes	1.27	1.37	-7%	[h]
1-C15E	1-Pentadecene	1.27	1.37	-7%	[h]
ME-FORM	Methyl Formate	0.064	0.06	6%	[h]
DGBE	2-(2-Butoxyethoxy)-Ethanol	2.87	2.70	6%	[h]
CL2-ME	Dichloromethane	0.066	0.07	-6%	[d]
N-C18	n-C18	0.44	0.47	-6%	[i]
48DM-C14	4,8-Dimethyl Tetradecane	0.55	0.58	-5%	[i]
N-C15	n-Pentadecane	0.53	0.56	-5%	[i]

- [a] The representation of the mechanism of this compound was changed. However, the mechanism is highly uncertain and the upper limit MIR probably should be used.
- [b] The "previous" value is the CARB staff's estimated upper limit MIR. The upper limit value should continue to be used in the regulation for consistency with the current policy for treatment of uncertainty.
- [c] The structure for this compound was incorrectly specified as that for 2,4,4-trimethyl-2-hexene when calculated previously.
- [d] Change due to round-off error, since the CARB tabulation had only two significant figures. The MIR's are the same to two significant figures.
- [e] The reason for this change could not be determined. This compound is represented using the lumped molecule method, and the calculated MIRs for the species used to represent it have not changed significantly.
- [f] The estimated mechanisms for organic acids have changed due to a modification in the estimation of branching ratios for the initial OH reaction at various positions around carboxylic acid groups.
- [g] Assignments for this compound could not be found on the previous databases.
- [h] The change for C₇ or the C₁₅ terminal alkenes is due to the change for 1-heptene or 1-pentadecene, respectively. The change for these higher molecular weight 1-alkenes must be due to some small change in the base mechanism or scenario assignments because the mechanism and the rate constants used are the same.
- [i] The reactivities of these compounds are expected to be highly sensitive to small changes in the base mechanism or scenario conditions. The mechanisms for these compounds were not changed.

Table 2. Listing of VOC compounds and categories that have been added to the list.

Model Name	Description	MIR (gm O ₃ / gm VOC)	Notes
BCYC-C8	C8 Bicycloalkanes	1.75	
13E5PCC6	1,3-Diethyl-5-Propyl Cyclohexane	0.96	
C3M2-C5E	Cis-3-Methyl-2-Pentene	12.84	
M-ET-TOL	m-Ethyl Toluene	9.37	
P-ET-TOL	p-Ethyl Toluene	3.75	
O-ET-TOL	o-Ethyl Toluene	6.61	
O-DE-BEN	o-Diethyl Benzene	5.92	[a]
M-DE-BEN	m-Diethyl Benzene	8.39	[a]
P-DE-BEN	p-Diethyl Benzene	3.36	[a]
1235MBEN	1,2,3,5 Tetramethyl Benzene	8.25	
INDENE	Indene	3.21	
ME-INDAN	Methyl Indans	2.83	
C12-TET	C12 Tetralin or Indane	2.33	
IAMOH	isoamyl alcohol (3-methyl-1-butanol)	2.73	
2ME1C4OH	2-methyl-1-butanol	2.60	[b]
MIBUCBN	4-methyl-2-pentanol (methyl isobutyl carbinol)	2.89	
23M1C5OL	dimethylpentanol (2,3-dimethyl-1-pentanol)	2.51	
1M1C7OL	5-methyl-1-heptanol	1.95	
TMCYC6OH	trimethylcyclohexanol	2.17	
26M2C7OH	dimethylheptanol (2,6-dimethyl-2-heptanol)	1.07	
26M4C9L	2,6-dimethyl-4-heptanol	2.37	
MENTHOL	menthol	1.70	
1-C10-OH	1-decanol	1.22	
37M1C8L	3,7-dimethyl-1-octanol	1.42	
268M4C9L	Trimethylnonanolthreoerythro; 2,6,8-Trimethyl-4-nonanol	1.55	
14-C4-OH	1,4-butanediol	3.22	
PNTAERYT	pentaerythritol	2.42	
2E13HXOL	2-Ethyl-1,3-hexanediol	2.62	
13DXOLAN	1,3-dioxolane	5.47	
14DXANE	1,4-dioxane	2.71	
IPIOIPR	diisopropyl ether	3.56	
EGDEE	ethylene glycol diethyl ether; 1,2-diethoxyethane	2.84	
ACETAL	acetal (1,1-diethoxyethane)	3.68	
44MHX3O	4,4-Dimethyl-3-oxahexane	2.03	
2M12M1MP	2-methoxy-1-(2-methoxy-1-methylethoxy)-propane	2.09	
3MEOC3OH	3-methoxy-1-propanol	4.01	
TH2FURM	tetrahydro-2-furanmethanol	3.54	
PROC3OH	n-propoxypropanol	3.84	
TEGLYCL	triethylene glycol	3.41	
DPGEE	dipropylene glycol ethyl ether	2.75	
TETGLCL	tetraethylene glycol	2.84	
1BOEO2PR	1-(butoxyethoxy)-2-propanol	2.08	
DBNP	glycol ether dpnb { 1-(2-butoxy-1-methylethoxy)-2-propanol }	1.96	
GBUTYACT	gamma- butyrolactone	1.15	
IPRFORM	Isopropyl Formate	0.42	
IAMACET	isoamyl acetate (3-methylbutyl acetate)	1.18	
2M1BACET	2-methyl-1-butyl acetate	1.17	
MAMACET	methyl amyl acetate (4-methyl-2-pentanol acetate)	1.46	
C5PROPAT	n-pentyl propionate	0.79	[b]

Table 2, continued

Model Name	Description	MIR (gm O ₃ / gm VOC)	Notes
5MC7-ACT	5-Methylheptyl Aceate	0.73	
MELAURAT	methyl dodecanoate {methyl laurate}	0.53	
ME-MYRST	methyl myristate {methyl tetradecanoate}	0.47	
MEOPRACT	methoxypropanol acetate	1.97	
12PGDACT	1,2-Propylene glycol diacetate	0.94	[b]
DPGNPE1	Dipropylene glycol n-propyl ether isomer #1	2.13	[b]
DPGMEA1	Dipropylene glycol methyl ether acetate isomer #1	1.41	[b]
DPGMEA2	Dipropylene glycol methyl ether acetate isomer #2	1.58	[b]
DPGMEA	Dipropylene glycol methyl ether acetate	1.49	[b]
GLY-ACET	glyceryl triacetate	0.57	
DIPRADP	diisopropyl adipate	1.42	
IBUTACD	isobutyric acid	1.22	
BUTACD	butanoic acid	1.78	
MALACD	malic acid	7.51	
3MBUTAC	3-Methylbutanoic acid	4.26	
ADIPACD	adipic acid	3.37	
HOPRACR	hydroxypropyl acrylate	5.56	
NBUACRAT	n-butyl acrylate	5.52	
IBU-ACRT	isobutyl acrylate	5.05	
ATRPNEOL	a-terpineol	5.16	
2MEXAL	2-methyl-hexanal	3.97	
MIPRK	Methyl Isopropyl Ketone	1.64	
24C5-K	2,4-pentanedione	1.02	
2PRCC6K	2-propyl cyclohexanone	1.71	
4PRCC6K	4-propyl cyclohexanone	2.08	
IBHK	2,6,8-trimethyl-4-nonanone; Isobutyl heptyl ketone	1.86	[b]
2M2C5E4O	mesityl oxide (2-methyl-2-penten-4-one)	17.37	
ISOPRON	isophorone {3,5,5-trimethyl-2-cyclohexenone}	10.58	
1C9E4ONE	1-nonene-4-one	3.39	
DOHACT	dihydroxyacetone	4.02	
C8-PHEN	C8 Alkyl Phenols	2.07	
C9-PHEN	C9 Alkyl Phenols	1.86	
C10-PHEN	C10 Alkyl Phenols	1.68	
C11-PHEN	C11 Alkyl Phenols	1.54	
C12-PHEN	C12 Alkyl Phenols	1.42	
EGPHE	2-Phenoxyethanol; Ethylene glycol phenyl ether	3.61	[b,c]
CCL4	Carbon Tetrachloride	0	
ME-BR2	Methylene Bromide	0	
C6-ALK	Unspeciated C6 Alkanes	1.48	
C7-ALK	Unspeciated C7 Alkanes	1.79	
C8-ALK	Unspeciated C8 Alkanes	1.64	
C9-ALK	Unspeciated C9 Alkanes	2.13	
C10-ALK	Unspeciated C10 Alkanes	1.16	
C11-ALK	Unspeciated C11 Alkanes	0.90	
C12-ALK	Unspeciated C12 Alkanes	0.81	
C13-ALK	Unspeciated C13 Alkanes	0.73	
C14-ALK	Unspeciated C14 Alkanes	0.67	
C15-ALK	Unspeciated C15 Alkanes	0.61	
C16-ALK	Unspeciated C16 Alkanes	0.55	

Table 2, continued

Model Name	Description	MIR (gm O ₃ / gm VOC)	Notes
C17-ALK	Unspeciated C17 Alkanes	0.52	
C18-ALK	Unspeciated C18 Alkanes	0.49	
C10-ARO	Unspeciated C10 Aromatics	5.48	
C11-ARO	Unspeciated C11 Aromatics	4.96	
C12-ARO	Unspeciated C12 Aromatics	4.53	
MS-802	Composite mineral spirit (naphthas or lactol spirits) (CARB Profile ID 802)	2.02	
MS-CP96	Thinning Solvent/Mineral Spirits (Cal Poly Slo. 1996)	1.99	
ISOPARM	Exxon Isopar(r) M Fluid	0.65	

[a] October 26 list had incorrect molecular weight.

[b] New model species added January 24, 2003

[c] Mechanism estimated as discussed in Footnote 101 in the revised Table C-1 available with the full reactivity tabulation at <http://www.cert.ucr.edu/~carter/reactdat.htm>.