Appendix B

Reactivity Scientific Advisory Committee Peer Review

CALIFORNIA INSTITUTE OF TECHNOLOGY
DIVISIONS OF CHEMISTRY AND CHEMICAL ENGINEERING
AND
ENGINEERING AND APPLIED SCIENCE

JOHN H. SEINFELD
LOUIS E. NOHL PROFESSOR

July 7, 2003

Mr. Bart Croes, Chief
Research Division
California Air Resources Board
1001 I Street
Sacramento, CA 95814

Dear Bart,

The ARB Reactivity Scientific Advisory Committee (RSAC) has reviewed the proposed amendments to the table of MIR values prepared by Dr. William P.L. Carter. The amendments do not substantially change the nature of the MIR values. In addition, the RSAC finds that the updated values were arrived at in an appropriate scientific manner.

Sincerely,

John H. Seinfeld

JHS:ah

cc: D. Luo

MAIL CODE 210-41, PASADENA, CALIFORNIA 91125

TELEPHONE (626) 395-4635 FAX (626) 796-2591 E-mail: seinfeld@caltech.edu

Subject: **Reactivity Scientific Advisory Committee (RSAC)**
Date: Fri, 27 Jun 2003 13:56:48 -0700
From: Dongmin Luo <dluo@arb.ca.gov>
Organization: California Air Resources Board
To: Roger Aktinson <roger.atkinson@ucr.edu> , Ted Russell <trussell@ce.gatech.edu> , seinfeld <seinfeld@caltech.edu> , Jack Calvert <calvert@acd.ucar.edu> , Harvey Jeffiries <harvey@unc.edu> , Jana Milford <milford@spot.colorado.edu>
CC: "McCauley, Eileen" <emccaule@arb.ca.gov> , "Corey, Richard" <rcorey@arb.ca.gov> , Bart Croes <bcroes@arb.ca.gov>

Dear RSAC member,

The purpose of this letter is to request your assistance with determining the appropriate level of peer review of information concerning an update to Maximum Incremental Reactivity (MIR) values. Specifically, we have attached a package that the ARB sent to Prof. John Seinfeld at Caltech on June 9, 2003, requesting the RSAC's assessment of the scientific portion of proposed amendments to the" Tables of Maximum Incremental Reactivity (MIR) Values" used in the aerosol coating regulation. The scientific portion was provided by Dr. William Carter at University of California, Riverside at the request of the Air Resources Board. After considering our request, Prof. Seinfeld directed us to forward the package to you. After providing some additional background, we identify the specific peer review options for which we are seeking your recommendation.

As you know, the Board adopted a regulation in June 2000 for reducing the ozone formed from aerosol coating emissions by establishing reactivity-based volatile organic compound (VOC) limits based on the MIR scale. Because the chemical mechanism is evolving as new information becomes available, the Board directed staff to review the "Tables of MIR Values" used in the aerosol coating regulation every 18 months after the effective date of the amendments (July 18, 2001), and every 18 months thereafter, to determine if modifications to the MIR values are warranted. In October 2002, we requested Dr. Carter to give us an update on the chemical mechanism as well as MIR values.

In February 2003, Dr. Carter provided an updated list of MIR values for our regulatory needs and stated that the updated MIR values had some differences from those submitted to the ARB in 2000. The differences were less than 5 percent for most of those species but are greater than 5 percent for a small number of the species, although the changes in most cases are well within the uncertainty of the estimates. As indicated in his letter (attached), there have been no significant changes to the SAPRC-99 mechanism since the MIR values incorporated in the current aerosol coating regulation were calculated. Generally, the changes are due to corrections and improvements to some mechanisms, emissions assignments or some of the files and software programs. In addition, the updated list includes 106 new VOC species.

Based on Dr. Carter's review and consultation with stakeholders, the ARB has concluded that modifications to the "Tables of MIR Values" should be pursued. However, because the proposed amendments are premised from a "scientific basis", an external scientific peer review is required by the Health and Safety Code 57004 for the scientific portion of the proposed amendments, i.e., updated MIR values.

Therefore, we again request your assistance in this peer review process. Please review the attached package and make a recommendation to Prof. Seinfeld on the appropriate level of peer review as well as any comments you may have. There are three possible levels of peer review:

1) As was done for the initial regulation, ARB could contract with a scientist to perform an in-depth peer review of the changes to SAPRC-99

since Dr. William Stockwell's peer review.

2) Convene a meeting of RSAC members via conference call with Dr. Carter to discuss the changes to the "Tables of MIR Values". The conference call might need to be notified as a public meeting.

3) If the committee agrees with the characterization that the changes are minor, individual review by RSAC members of the attached description will constitute the peer review.

It would be appreciated if you can send your recommendations concerning which of the options identified above as well as any other comments to Prof. Seinfeld at seinfeld@caltech.edu by July 7, 2003.

If you have any questions or need additional information, Please contact me at (916) 324-8496 or dluo@arb.ca.gov. Thank you again for your efforts to assist us with ensuring that the ARB uses the most current, scientifically sound tools to support its programs.

Sincerely,

Dongmin Luo
ARB Reactivity program coordinator

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Dongmin Luo, Ph.D., P.E.
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RSAC package.pdf	**Name:** RSAC package.pdf **Type:** Acrobat (application/pdf) **Encoding:** base64 **Download Status:** Not downloaded with message

Winston H. Hickox
Agency Secretary

Air Resources Board

Alan C. Lloyd, Ph.D.
Chairman
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Gray Davis
Governor

June 9, 2003

Professor John H. Seinfeld
California Institute of Technology 210-41
1200 E. California Boulevard
Pasadena, CA 91125

Dear Professor ~~Seinfeld~~ John:

This is to request the Reactivity Scientific Advisory Committee (RSAC)'s assessment on the scientific portion of proposed amendments to the Tables of Maximum Incremental Reactivity (MIR) Values used in the aerosol coating regulation (Title 17, Sections 94700 and 94701). The scientific portion was provided by Dr. William Carter at the University of California, Riverside at the request of the Air Resources Board (ARB).

As you may recall, the RSAC met in October 1999 to discuss reactivity-related issues. At the meeting, the Committee accepted the review performed by Dr. William Stockwell on the chemical mechanism (SAPRC-99) used in the MIR scale. The RSAC also endorsed the use of the mechanism as representing the state-of-the-art in urban atmospheric chemical reaction mechanisms.

Consequently, the Board adopted a regulation in June 2000 for reducing the ozone formed from aerosol coating emissions by establishing reactivity-based volatile organic compound (VOC) limits for aerosol coatings based on the MIR scale. Because the chemical mechanism is evolving as new information becomes available, the Board directed staff to review the Tables of MIR Values used in the aerosol coating regulation every 18 months after the effective date of the amendments (July 18, 2001), and every 18 months thereafter, to determine if modifications to the MIR values are warranted. In October 2002, we requested Dr. Carter to give us an update on the chemical mechanism as well as MIR Values.

In February 2003, Dr. Carter provided an updated list of MIR values for our regulatory needs (enclosure 1) and stated that the updated MIR values had some differences from those submitted to the ARB in 2000. The differences were less than 5 percent for most of those species but are non-negligible for a small number of the species, although the changes in most cases are well within the uncertainty of the estimates (enclosure 2). As indicated in his letter, there have been no significant changes to the SAPRC-99 mechanism since the MIR values incorporated in the current aerosol coating regulation were calculated. Generally, the changes are due to corrections and improvements to

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California Environmental Protection Agency

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some mechanisms, emissions assignments or some of the files and software programs. In addition, the updated list includes 106 new VOC species, for which MIRs have been calculated.

Based on Dr. Carter's review and consultation with stakeholders, the ARB has concluded that modifications to the Tables of MIR Values should be pursued. However, because the proposed amendments are premised from a "scientific basis", an external scientific peer review is required by the Health and Safety Code 57004 for the scientific portion of the proposed amendments, i.e., updated MIR values.

Therefore, we again request your assistance in this peer review process. Specifically, we request that the RSAC review Dr. Carter 's work for our regulatory needs. To expedite the process, we'd like to suggest that we distribute the materials provided by Dr. Carter to the members of the RSAC and solicit the committee's input to determine the appropriate level of peer review. It would be appreciated if we can receive your letter of recommendation by the end of June 2003.

If you have any questions regarding this request, please contact me at (916) 323-4519 or bcroes@arb.ca.gov, or Dr. Dongmin Luo of my staff at (916) 324-8496 or dluo@arb.ca.gov.

Sincerely,

Bart E. Croes, P.E., Chief
Research Division

Enclosures

cc: Dongmin Luo, Ph.D., P.E.
Research Division

UNIVERSITY OF CALIFORNIA, RIVERSIDE

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RIVERSIDE, CALIFORNIA 92521-0434

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 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.

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 C_7 or the C_{15} 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	
IPROIPR	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	[illegible]	
MAMACET	methyl amyl acetate (4-methyl-2-pentanol acetate)	1.46	

Table 2, continued

Model Name	Description	MIR (gm O_3 / gm VOC)	Notes
C5PROPAT	n-pentyl propionate	0.79	[b]
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	0.72	
C14-ALK	Unspeciated C14 Alkanes	0.67	

Table 2, continued

Model Name	Description	MIR (gm O_3 / gm VOC)	Notes
C15-ALK	Unspeciated C15 Alkanes	0.61	
C16-ALK	Unspeciated C16 Alkanes	0.55	
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 wit the full reactivity tabulation at http://www.cert.ucr.edu/~carter/reactdat.htm.

Enclosure 2

On May 21, 2003 Bill Carter wrote:

As you requested, I reviewed the changes to the MIR scale that were discussed in my letters to Mr. Richard Corey of the CARB earlier this year. As indicated there, there have been no significant changes to the SAPRC-99 mechanism since I submitted the final version of the SAPRC-99 report in May of 2000. However, as also discussed in that letter, some MIR's changed when they were recomputed earlier this year for the CARB's regulatory update. The reasons for these changes were discussed in the letter and further discussed below.

Although the vast majority of compounds had no changes in their mechanisms and no changes were made to the base mechanism, the MIRs calculated early this year for the regulatory update had some small differences from those that were submitted to the CARB in 2000. The differences were <5% for almost all of those species, except for a few highly scenario-sensitive species whose MIRs are particularly scenario-sensitive, where the differences were larger (<12%), though still relatively small. A comparison of the O3 results in the scenario calculations with no added VOC indicated no differences in the base case scenarios, but small (<=~2%) differences for the MIR scenarios. This is apparently due to a change made to the program that computes MIR levels by varying NOx inputs to find which conditions give maximum base ROG incremental reactivities. The differences in NOx levels that yield MIR conditions between the two versions of the pro gram are also on the order of 2% or smaller. This probably represents the numerical uncertainty of the calculations that determine MIR NOx levels. The resulting differences in MIRs can probably also be considered to be within the numerical uncertainty of the MIR calculation.

I have also found that although the results of the calculations of the base case scenarios did not change, there are differences in calculated incremental reactivities for these scenarios on the same order of the differences in MIRs. This may be due to some changes in the reactivity calculation software that was made in the intervening period. It would take significant effort to identify and explain the exact source(s) of the changes. I do not think this would accomplish much since the changes are within the uncertainty of the calculation, and it is more likely that the program changes were improvements, since if I didn't think so I wouldn't have made them.

Some VOCs had mechanisms or representations changed since the periods of the two MIR calculations, which resulted in corresponding MIR changes. These cases are noted in footnotes to the table in the letter summarizing changes in MIRs. The biggest MIR change is for 2-(chloromethyl)-3-chloropropene, a VOC whose mechanism is so uncertain that upper limit MIRs should be used in any case, and which is only on the list because we used it in some experiments and is not in any emissions inventory that I know of. The next two largest changes are for amines where the CARB had upper limit estimates on their table and I had "best estimate" MIRs. However, as noted on the table footnote, these "best estimates" are so uncertain that use of upper limits is probably still more appropriate.

The next largest change is for methane, where the difference between my value and that on the CARB table is entirely due to roundoff error on the CARB table. Round-off error also explains changes for some other very low reactivity compounds on the list.

The reason for the ~35% change for the "C15 cycloalkanes" lumped species could not be determined without spending considerably more time on this that

I consider worthwhile. Considering the uncertainties both in the appropriate set of species to represent this and the estimated mechanisms for these species, this is well within the uncertainty in the MIR for compounds represented by this species.

The changes in the MIR's for acetic acid and other carboxylic acids was due to changes in the mechanism estimation system for reactions about the carboxylic acid group, as indicated in the footnote. The documentation output by the mechanism generation system for acetic acid is given below.

I was unable to determine the reason for the MIR change for the Dipropylene Glycol Methyl Ether isomer (2-[2-methoxypropoxy]-1-propanol) since I couldn't find it on the previous database. It may be be that a different isomer was represented previously. In any case, I think the MIR in the latest list is appropriate for the structure indicated.

The other changes are less than 10% and are probably due primarily to the program changes specified above.

I hope this discussion is sufficient. If you require a detailed examination of why all changes occurred, considerable additional effort would be required that I frankly think would be better spent on other priorities. A peer review at the level of detail relevant to the factors discussed above would also be quite expensive and probably also not worth the effort, considering that in most cases the changes are well within the uncertainty of the estimates, and in most others the changes are probably due to corrections or other improvements.

- Bill Carter

Generated mechanism for acetic acid:

OH Reaction Documentation

Assigned reactions for CH3-CO-OH (100.0%)

CH3-CO-OH + OH -> H2O + HO-CO-CH2. (1)
Assumed to occur 13.0% of the time, independent of temperature (13.0%)
Branching ratio based on ratio of estimated rate constant for reaction at this route to total OH radical rate constant.
Total k= 8.00e-13 independent of temperature.
k for T=298 only. Assumed to be temperature-independent.
Atkinson (1994)

CH3-CO-OH + OH -> H2O + CH3-CO2. (2)
Assumed to occur 87.0% of the time, independent of temperature (87.0%)
Most of the reaction is believed to occur at this position (Atkinson et al, IUPAC Evaluation, 1999).

Nitrate yield from HO-CO-CH2OO. (13.0%)

HO-CO-CH2OO. + NO -> HO-CO-CH2-ONO2 (4)
Best fits to observed or adjusted nitrate yields for most of the few primary, tertiary, or substituted peroxy radicals where data are available is obtained by reducing the effective carbon number by 1.5.
Only lowest group carbon number reduction used.

Zero nitrate yield assumed for effective nC = 0.5
Nitrate yield = 0.0%.

Alkoxy reactions for HO-CO-CH2O. (13.0%)

HO-CO-CH2O. + O2 -> HCO-CO-OH + HO2. (5)
O2 reaction (T= 300K, 20.9% O2): k*[O2]= 3.29e+3 s-1 (100.0%)
k(300)= 6.42e-16 cm3 molec-1 s-1.
A factor assumed to be the same as for CH3-CH2O. Ea estimated using linear relationship between Ea and heat of reaction for methoxy, ethoxy, and isopropoxy, assuming minimum activation energy of 0.40 kcal/mol.
k= A*e^-Ea/RT; A= 6.00e-14 cm3 molec-1 s-1; Ea= max(0.4, Ea[est]);
Ea[est]= 6.96+0.183*Hr = 2.71 kcal/mol; Hr= -23.25 kcal/mol.
[C_(CO)(O*): Alcohols forming this radical are assumed to have the same O..H bond dissociation energy as CH3-CH2-CH2-O..H Note that this depends on highly uncertain assignment for C_(CO)O.]

HO-CO-CH2O. -> HCHO + HO-CO. (6)
Decomposition (T= 300K): k= 2.19e+1 s-1. (0.7% =~0%)
k= A*e^-Ea/RT; A= 2.00e+14 s-1; A factor estimates based on recommendations of Atkinson (1994, 1996).
Ea = max [0.75 , EaA + EaB x Hr] = 17.79 kcal/mole. For reactions forming HO-CO.: EaA = 12.00, EaB = 0.44. Hr= 13.16 kcal/mol.
EaA and EaB adjusted to predict decomposition forming ROCO. dominates for CH3-C[O.](CH3)-CO-O-CH3 but is minor for CH3-O-CO-CH2-CH[O.]-CO-O-CH3, for model to predict reactivity data for both methyl isobutyrate and DBE-4.
[C_(CO)(O*): Alcohols forming this radical are assumed to have the same O..H bond dissociation energy as CH3-CH2-CH2-O..H Note that this depends on highly uncertain assignment for C_(CO)O.]
[O_(*CO): HCO-OH is assumed to have same (CO)..H bond dissociation energy as CH3-O-CHO.]
[*CO_(O): The C-H bond energy in formates is estimated to be 95 kcal/mole or higher based on an assumed correlation between bond the dissociation energy and CO-H + OH rate constants.]

Alkoxy reactions for CH3-CO2. (87.0%)

CH3-CO2. -> CO2 + CH3. (6)
Decomposition (T= 300K): k= 1.39e+7 s-1. (100.0%)
k= A*e^-Ea/RT; A= 2.00e+14 s-1; A factor estimates based on recommendations of Atkinson (1994, 1996).
Ea = max [0.75 , EaA + EaB x Hr] = 9.83 kcal/mole. For reactions forming CH3.: EaA = 14.05, EaB = 0.44. Hr= -9.60 kcal/mol.
EaA and EaB estimated from least squares fit of heat of reaction vs activation energies for such reactions with known or derived rate constants
[CO_(C)(O*): Derived from the IUPAC heat of formation for CH3COOH, and the CRC O..H bond dissociation energy.]