

ADDITIONS AND CORRECTIONS TO THE SAPRC-99 MAXIMUM INCREMENTAL REACTIVITY (MIR) SCALE

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Summary

The Maximum Incremental Reactivity (MIR) and other reactivity scales given by Carter (2000) has been recalculated after correcting minor errors in the mechanism generation system and to add several new compounds as requested by the California Air Resources Board and others. A total of 19 types of VOCs have been added, the MIRs for 11 VOCs changed by more than 2% but less than 10%, and the MIR for 2-methyl-2-butene-3-ol decreased by 24%. The changes and additions are summarized on Table 1, and the complete updated scale is available by ftp at <ftp://cert.ucr.edu/pub/carter/r99tab2.xls>.

Introduction

Volatile organic compounds (VOCs) can differ significantly in their impacts on ground-level ozone formation, and regulations that take these differences into account can potentially provide more efficient control of ozone than those that do not. In view of this, the California Air Resources Board (CARB) has adopted the Maximum Incremental Reactivity (MIR) scale of Carter (2000) as a means to quantify ozone impacts in its regulations of emissions of VOCs from aerosol coatings (CARB, 2000). This scale is derived using computer model calculations of incremental ozone impacts of VOCs under in a set of scenarios representing conditions where ozone is most sensitive to VOC emissions (Carter, 1994, 2000), with the atmospheric reactions of the VOCs represented using the SAPRC-99 chemical mechanism (Carter, 2000). The mechanisms for many of the VOCs were derived using an automated mechanism generation system employing various estimation methods to estimating branching ratios for various competing reactions. The report of Carter (2000) gives tabulated MIR values for approximately 400 types of VOCs, accounting for most of the major types of VOCs present in current emissions inventories.

Since the time the report of Carter (2000) was finalized, some minor corrections and updates were made to the SAPRC-99 mechanism generation system, resulting in slightly modified mechanisms for some VOCs. In addition, the CARB staff requested that several additional VOCs be added to the MIR tabulation for use in the aerosol coatings regulations, and the addition of a few other VOCs were requested by others. Although it was not possible to add all the VOCs that were requested without

Table 1. Listing and MIRs of VOC species added to the mechanism or whose MIR's have changed by more than 2% since the last update, and other corrections to the current tabulation.

Model Species Name	Description	CAS No.	Molecular Weight	Updated MIR [a]	Previous MIR [b]	Unc [c]
2346TMC7	2,3,4,6-Tetramethyl Heptane		156.31	1.26		3
2357TMC8	2,3,5,7-Tetramethyl Octane		170.34	1.06		3
2468TMC9	2,4,6,8-Tetramethyl Nonane		184.37	0.94		3
236M4IC7	2,3,6-Trimethyl 4-Isopropyl Heptane		184.37	1.24		3
24568MC9	2,4,5,6,8-Pentamethyl Nonane		198.40	1.11		3
2M35IPC7	2-Methyl 3,5-Diisopropyl Heptane		198.40	0.78		3
268M4IC9	2,6,8-Trimethyl 4-Isopropyl Nonane		212.42	0.76		3
27M35IC8	2,7-Dimethyl 3,5-Diisopropyl Heptane		226.45	0.69		3
1-C14E	1-Tetradecene		196.38	1.41	1.48	4
C14-OLE1	C14 Terminal Alkenes		196.38	1.41	1.48	4
1-C15E	1-Pentadecene		210.41	1.37	1.30	4
C15-OLE1	C15 Terminal Alkenes		210.41	1.37	1.30	4
C8-BEN2	C8 Disubstituted Benzenes	1330-20-7	106.17	7.48	5.16 [d]	3
C8-BEN [d]	Isomers of Ethylbenzene		106.17	5.16	5.16	3
I-C10-OH	8-Methyl-1-Nonanol (Isodecyl Alcohol)	25339-17-7	158.29	1.23	1.18	3
22MEOC3	2,2-Dimethoxy Propane	77-76-9	104.15	0.52		3
DPRGOME [e]	Dipropylene Glycol Methyl Ether isomer (1-methoxy-2-[2-hydroxypropoxy]-propane)		148.20	2.20	2.20	3
DPGOME2 [e]	Dipropylene Glycol Methyl Ether isomer (2-[2-methoxypropoxy]-1-propanol)	34590-94-8	148.20	3.02		3
TMPDG	2,2,4-Trimethyl-1,3-Pentanediol	144-19-4	146.23	1.74		3
ME-FORM	Methyl Formate	107-31-3	60.05	0.06	0.07	3
IPR-ACET	Isopropyl Acetate	108-21-4	102.13	1.12	1.24	2
ME-PVAT	Methyl Pivalate	598-98-1	116.16	0.39	0.41	2
TBU-ACET	t-Butyl Acetate	540-88-5	116.16	0.20	0.22	2
IBU-IBTR	Isobutyl Isobutyrate	297-85-8	144.22	0.61	0.64	3
DBE-4	Dimethyl Succinate	106-65-0	146.14	0.23	0.25	3
DBE-5	Dimethyl Glutarate	1119-40-0	160.17	0.51	0.49	3
DBE-10	Dimethyl Sebacate	106-79-6	230.31	0.48		3
GLYACD	Glycolic Acid	79-14-1	76.05	2.67		3
MACRACD	Methacrylic Acid	79-41-4	86.09	18.78		5
2ETHXACD	2-Ethyl Hexanoic Acid	149-57-5	114.22	4.41		3
MBUTENOL	2-Methyl-2-Butene-3-ol	34454-78-9	86.13	5.12	4.12 [f]	3
2ETHXACR	2-Ethyl-Hexyl Acrylate	103-11-7	184.28	2.42		5
5M2HXO	5-Methyl-2-Hexanone	110-12-3	114.19	2.10		3
3M2HXO	3-Methyl-2-Hexanone	2550-21-2	114.19	2.81		3
DMSO	Dimethyl Sulfoxide	67-68-5	78.13	6.90		2

[a] Maximum incremental reactivity in units of grams O₃ per gram VOC. Calculation of 11/13/2000.

[b] MIR given in tabulation dated May 8, 2000. If blank, then this VOC was added to the list since then.

[c] Uncertainty codes have the same meanings as in the previous tabulations.

[d] In the previous tabulation, "Isomers of Ethylbenzene" was incorrectly given the same model species name as used for "C8 Disubstituted Benzenes". This resulted in the reactivity tabulation software incorrectly giving the C8 disubstituted benzenes the MIR calculated for isomers of ethylbenzene, which is lower because ethylbenzene is included in the average. This has been corrected by giving the isomers of ethylbenzene a different model species name.

[e] The previous tabulation used a different structure for dipropylene glycol methyl ether (DPRGOME) than is associated with this name on the ChemFinder database. A new model species (DPGOME2) is added for the latter isomer.

[f] This 25% change is due to correcting an error in the assigned carbon number for this compound. The mechanism for the compound is unchanged.

additional funding for this purpose, it was possible to add most of the requested VOCs to the SAPRC-99 mechanism without significant effort.

Because of this, the MIR and the other reactivity scales given by Carter (2000) were recalculated, and the updated scale is now available at by ftp at ftp.cert.ucr.edu/pub/carter/r99tab2.xls. (This will be linked to the Carter reactivity web site once the ARB has reviewed the revised data.) The VOC classes that were added to the mechanism or whose MIRs changed by more than 2% are listed on Table 1. The table also gives the current and (if applicable) previous calculated MIRs, the uncertainty classifications using the codes of Carter (2000), and other information for these species. The changes and additions are discussed in more detail below.

Mechanism Corrections and Modifications

Estimations of Ester Rearrangements

The ester rearrangement is a decomposition reaction that can be undergone by alkoxy radicals formed in the photooxidations of compounds with ester groups, which occurs via the general mechanism



Carter (2000) describes a way to estimate that rate constant, based on available mechanistic data concerning methyl acetate (Christensen et al, 2000) and other compounds. However, a transcription error gave an incorrect value for the product yield data of Christensen et al (2000), resulting in inappropriate estimates for branching ratios for some cases. Appendix A to this report has the corrected text of the portions of the Carter (2000) report concerning estimation of rate constants for this reaction.

Because of the nature of the error, the effect on the estimated mechanism is generally negligible except for some methyl esters, and even for those the error causes less than a 10% change in the calculated MIR. As shown on Table 1, the compounds whose MIRs are most affected are isopropyl acetate and dimethyl succinate, whose MIRs were reduced by 9% and 6%, respectively.

Other Modifications

Some minor modifications were made that were not expected to significantly affect generated mechanisms. These changes and perhaps numerical imprecisions in the calculations resulted in MIRs changing by small amounts in some cases, though most changes in MIRs for compounds without known mechanism modifications were less than 2%, and all were less than 5%.

The parameter file used to specify carbon numbers was found to give an incorrect carbon number of 4 for 2-methyl-2-butene-3-ol, instead of the correct value of 5. Because of the way the MIRs were calculated, this resulted in 25% error in the calculated MIR for that compound in the previous tabulation. A naming problem for the model species used to represent unspeciatiated C8 aromatics caused the tabulation program to give an incorrect MIR tabulated for the unspeciatiated xylene isomers. These have been corrected.

Compounds Added

A total of 19 compounds have been added to the SAPRC-99 mechanism since the report of Carter (2000) was completed, allowing them to be added to the MIR and other reactivity scales. These include the following:

- Several highly branched C_{≥11} alkanes were added to the mechanism as part of our study of the reactivity of Isopar® fluids we carried out for ExxonMobil corporation (Carter et al, 2000a). These were included in a hypothetical surrogate mixture derived to represent Isopar-M® fluid. The mechanisms for these compounds were derived using the SAPRC-99 mechanism generation system (Carter, 2000). These are assigned to uncertainty class “3”, as was done for the other high molecular weight alkanes.
- Several oxygenated compounds were added as the request of the CARB or others, or because they were found to be present in various mixtures whose reactivities the author was requested to assess. The mechanisms for these compounds were also derived using the SAPRC-99 mechanism generation system (Carter, 2000). Except for methacrylic acid, these were assigned uncertainty class “3”, as was done for similar oxygenated compounds whose mechanisms were estimated. The ability of the mechanism generation system to accurately derive mechanisms for acrylates and similar unsaturated oxygenates is uncertain, so methacrylic acid was assigned uncertainty class “5”.
- A second isomer of “dipropylene glycol methyl ether” was added with a structure given for that compound on the ChemFinder database.
- Dimethyl sulfoxide was added, using on a mechanism recently derived based on a recent experimental study of the reactivity of the compound (Carter et al, 2000b). Although the mechanism has some uncertainties, it was reasonably well tested using chamber data, so it is given an uncertainty classification of “2”.

Compounds Not Added

The ARB also requested that we calculate MIRs for several compounds whose mechanisms are unknown and which could not be derived using the existing SAPRC-99 mechanism generation system. Because of resource limitations we did not attempt to derive mechanisms for these compounds, and thus their MIRs were not derived. These included the following types of compounds

- Amines, Oximes, Nitro compounds, etc. Mechanisms for the atmospheric reactions of such compounds have not been derived, nor are methods available to estimate their mechanisms. Thus the amines dexpanthenol, n-methylacetamide, triethyl amine, 2-amino-2-methyl-1-propanol, diethylenetriamine, hydroxyethylethylene urea, 1-amino-2-propanol, and morpholine, the nitro compounds nitroethane, nitromethane, 1-nitropropane, and 2-nitro-propane, and the oxime ethyl methyl ketone oxime could not be added.
- Halogenated Organics. The current SAPRC-99 mechanism does not support reactions of halogen species. The results of the few reactivity studies of halogenated compounds that have been carried out indicate that their reactions involve processes that are not well represented even in mechanisms that attempt to include their reactions (Carter et al, 1996, 1997; Carter and Tuazon, 2000). Thus 1,1,1,2-Tetrafluoroethane, and 1,1-Difluoroethane could not be added. However, it should be noted that the reactivities of these compounds are expected to be extremely low.
- Bicyclic compounds. The current SAPRC-99 mechanism generation system cannot automatically generate mechanisms for compounds with more than one ring. The amount of effort required to derive estimated mechanisms manually, or to upgrade the software of the system to so it can process such compounds, is beyond the scope of this project. Thus isobornyl methacrylate could not be added.
- Hydroperoxides. The ARB requested that cumene hydroperoxide and peroxyacetic acid be added. The current system cannot automatically process mechanisms for aromatics or hydroperoxides, so mechanisms for these compounds would have to be derived manually.

It may be possible to derive approximate or “best estimate” mechanisms for some of these compounds, but this would require a level of effort that is beyond the scope of existing CARB projects. Reasonable estimates for the hydroperoxides and nitro compounds may be possible with a relatively modest level of effort, and “placeholder” mechanisms for amines and some halogenated compounds could be derived if methods to estimate their OH rate constants are developed or applied.

References

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APPENDIX A
CORRECTED DISCUSSION OF ESTER REARRANGEMENT
IN SAPRC-99 MECHANISM DOCUMENTATION

III.J. Reactions of Alkoxy Radicals

5. Ester Rearrangement

Tuazon et al (1998b) and Christensen et al (2000) recently reported data indicating that α -ester-substituted alkoxy radicals undergo a second type of hydrogen shift isomerization, where the hydrogen α to the alkoxy center shifts, via a 5-member ring transition state, to the ester carbonyl oxygen atom, forming an acid and an acyl radical, e.g.,



In order to account for the product data in the reactions of OH + methyl (Christensen et al, 2000) and ethyl (Tuazon et al, 1998b) acetates, it is necessary to assume that this "ester rearrangement" reaction occurs at a non-negligible or rapid rate. Therefore, this reaction must be taken into account when generating mechanisms for esters.

The available data give some limited information upon which to base quantitative estimates for the rate constants for these reactions. In the case of the alkoxy radical formed from methyl acetate [$\text{CH}_3\text{-CO-O-CH}_2\text{O}\cdot$], the product data reported by Christensen et al (2000) indicated that the ester rearrangement occurs at a rate that is about 1.86 times that of the competing reaction with O_2 under ambient conditions. Based on the 298K rate constant for the reaction of O_2 with this radical estimated as discussed in Section III.J.1, this gives a 298K rate constant for the ester rearrangement to be $5.0 \times 10^4 \text{ sec}^{-1}$. In the case of the radical formed from ethyl acetate [$\text{CH}_3\text{CH(O}\cdot\text{)O-CO-CH}_3$], the data of Tuazon et al (1998b) indicate that the ester rearrangement dominates over the competing reactions of this alkoxy radical (primarily reaction with O_2 and decomposition to CH_3CHO and $\text{CH}_3\text{CO}_2\cdot$), which are estimated to have a total rate constant of $\sim 5 \times 10^4 \text{ sec}^{-1}$ under atmospheric conditions. This means that the ester rearrangement for this radical must have a rate constant of at least $\sim 3 \times 10^5 \text{ sec}^{-1}$ under ambient conditions. The differences in these two rate constants can be explained if it is assumed that the ester rearrangement rate constant depends on the heat of reaction. In particular, the ester rearrangement for the radical formed from methyl acetate is estimated to be endothermic by $\sim 3 \text{ kcal/mole}$, while the more rapid ester rearrangement of the radical formed from ethyl acetate is estimated to be endothermic by $\sim 8.4 \text{ kcal/mole}$.

To obtain a rough estimate of temperature dependence, we assume that these ester rearrangements have an A factor of $8 \times 10^{10} \text{ sec}^{-1}$, which is approximately the same as that used for 1,4-H shift isomerizations, based on expected similarities in the structure of the transition states. As with the decomposition reactions discussed above, the activation energy is assumed to linearly dependent on the heat of reaction, i.e.,

$$E_a(\text{ester rearrangement}) = E_a A^{\text{estr}} + E_a B^{\text{estr}} \cdot \Delta H_r \quad (\text{XXV})$$

where ΔH_r is the heat of reaction of the rearrangement. Obviously, the one quantitative rate constant derived from the methyl acetate data and the lower limit from the ethyl acetate data are insufficient to uniquely determine $E_a A^{\text{estr}}$ and $E_a B^{\text{estr}}$. However, the results of the environmental chamber reactivity experiments for n-butyl acetate (Carter et al, 2000a; see also Section V.B) can only be fit by model

simulations if the ester rearrangement for $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{O}\cdot)\text{-O-CO-CH}_3$ (radical 26 on Table 33) is of comparable rate or slower than the competing isomerization to $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{-O-CO-CH}_3$, which means that this ester rearrangement, with an estimated ΔH_r of -8.1 kcal/mole, should have an estimated 298K rate constant of $\sim 3 \times 10^5 \text{ sec}^{-1}$ or less. To be consistent with this as well as the methyl and ethyl acetate product data discussed above, we assume that

$$EaA^{\text{estr}} = 9.11 \text{ kcal/mole}$$

and

$$EaB^{\text{estr}} = 0.20,$$

which yields

$$k(\text{ester rearrangement}) = 8 \times 10^{10} e^{-(9.11+0.2 \Delta H_r)/RT} \quad (\text{XXVI})$$

Obviously, this is highly uncertain, and more quantitative information concerning relative rates of competing reactions involving this rearrangement, or at least more upper or lower limit data, would significantly reduce the uncertainty of these estimates.

Tuazon et al (1998b) saw no evidence that the analogous ester rearrangement reaction involving a 6-member ring transition state that might be expected to occur in the t-butyl acetate system, e.g.,



in fact occurs to any significant extent. Of course, this could be because the competing decomposition to $\text{HCHO} + \text{CH}_3\text{C}(\cdot)(\text{CH}_3)\text{-O-CO-CH}_3$ is predicted to be very fast, with an estimated rate constant of $\sim 3 \times 10^7 \text{ sec}^{-1}$. Nevertheless, we tentatively assume that these reactions are not important, and the possibility that they may occur is not presently incorporated in the mechanism generation system. However, the possibility that this occurs needs to be investigated.

VIII. References

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