

Estimation of Ozone Reactivities for Volatile Organic Compound Speciation Profiles in the Speciate 4.2 Database

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Summary

Incremental reactivities for ground-level ozone formation were assigned for all volatile organic compound (VOC) emissions profiles in the Speciate 4.3 database. Best estimate and upper and lower limit reactivity values are given for the maximum incremental reactivity (MIR), maximum ozone incremental reactivity (MOIR) and equal benefit incremental reactivity (EBIR) calculated using the latest version of the SAPRC-07 chemical mechanism. The results are given in an Excel spreadsheet included as an appendix to this report. Estimates were made for compounds for which no reactivity data are available, and methods were developed to derive upper, lower, and estimated reactivity values for poorly defined or unspciated VOC categories. The upper and lower reactivity estimates reflect only uncertainties in making reactivity assignments to the chemical categories used in the Speciate database and not reactivity values for individual chemical compounds and uncertainties in how the profiles were developed. The methods employed and the uncertainties in the results are discussed in this report.

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Introduction

Many hundreds of types of volatile organic compounds (VOCs) are emitted into the atmosphere, where their gas-phase reactions in the presence of oxides of nitrogen (NO_x) may participate in the formation of ground-level ozone, which is an air problem in many regions (NRC, 1991; Findlayson-Pitts and Pitts, 1999). Each VOC differs in its effect on ground-level ozone formation, and this into account can potentially lead to more efficient VOC control strategies to reduce ozone. The ozone impact of a VOC can be quantified by its *incremental reactivity*, which is defined by the change in ozone caused by adding a small amount of the VOC to the emissions, divided by the amount of VOC added. Incremental ozone reactivities depend on the environment where the VOC is emitted, and various reactivity scales have been developed to reflect these conditions. For example, Carter (1994) developed the Maximum Incremental Reactivity (MIR) scale to reflect relatively high NO_x conditions where ozone formation is most sensitive to VOC emissions, the Maximum Ozone Incremental Reactivity (MOIR) scale to represent lower NO_x conditions that give the highest ozone concentrations, and the Equal Benefit Incremental Reactivity (EBIR) scale to represent yet lower NO_x conditions where NO_x control and VOC control are equally effective in reducing ozone formation. Because the MIR scale reflects conditions where VOC control is most effective, it is generally the most widely used in VOC reactivity assessments and is the basis for several reactivity-based regulations in California (e.g., CARB 1993, 2000). However, the MOIR or EBIR scales may be more representative of regional environments where ozone formation is more controlled by the availability of NO_x.

For regulatory assessments and modeling purposes, VOC emissions are generally not given in terms of emissions of individual compounds, but instead are given in terms of mass emissions of various types of source categories, such as various types of vehicle evaporations or exhausts, solvents, industrial processes or consumer products. For air quality modeling to assess ozone impacts, the actual compounds from these emissions sources are given in *speciation profiles* that are assigned to each source. These give mass fractions of various types of VOC compounds or mixtures in these various sources. These profiles are then used when preparing emissions data for air quality modeling, where they are used to determine how to represent these emissions for modeling purposes (e.g., see Carter 2013a for assignments of the lumped species used in various airshed models to chemical categories used in various speciation profile databases).

Most of the latest VOC speciation profiles currently in use have been compiled and incorporated in the U.S. EPA's Speciate database (EPA, 2012), of which the latest version is Speciate 4.3, which was last updated September, 28, 2011. This database contains 1775 profiles that represent VOC emissions, each containing mass fractions of VOCs organized into 1797 chemical categories¹. Although most (61%) of these categories refer to single compounds, a non-negligible number of categories refer to mixtures of compounds (25%) or mixtures of unknown composition or compounds that have not yet been categorized (14%). However, if the mass of each profile is weighed equally, only 8% of the mass consists of mixtures whose chemical compositions could not be derived, and only 0.002% of the mass consists of compounds that have not been assigned to explicit or lumped chemical categories used in airshed models (Carter, 2013a). Although the various profiles differ significantly in terms of their contributions to the total mass of VOC emissions into any air basin, generally the most important profiles tend to be better characterized, so the contributions of unknown or unassigned categories are expected to be even lower.

Although the primary use of speciation profiles is for processing emissions from various sources for use in airshed models for assessing effects of these sources on air quality, an indication of the ozone impacts of these sources can also be assessed without the need to carry out such modeling. If incremental

¹ The Speciate database actually has more VOC categories, but those that are not used in any profile in the database are ignored in this discussion.

reactivities such as MIR values could be assigned to each profile, then one has an indication of the relative impacts of the various emissions sources in terms of relative amounts of ozone formed from each source per unit mass emitted. This combined with the mass emissions of the source, gives an indication of the relative impact of the source on ozone formation. Of course ozone impacts depend on the environment where the VOC reacts, so in principle a reactivity scale analysis would not be as accurate as modeling the effects of the source, though in practice there are uncertainties in the model inputs and almost all models use lumped chemical mechanisms with introduce uncertainties of their own. In any case, this approach can at least provide a relatively easy to use alternative to complex modeling for assessment purposes.

However, assigning reactivity values to the profiles is not as straightforward as it seems. Although the average unknown mass in the profiles is only ~8%, some profiles (and therefore VOC emissions sources) have significantly higher unknown fractions, ranging up to over 80%. In addition, although the most important compounds generally have MIR and other reactivity values, a large number of compounds, making up a non-negligible mass of all profiles and most of the mass in some profiles, do not have reactivity values assigned. Unless some means can be developed to make at least upper and lower limit reactivity estimates for the unknown or unassigned mass in the profiles, then many profiles will not have reactivity values, which would limit the utility of this method.

In this project, we developed methods to make best estimate and upper and lower limit reactivity estimates for the full range of compounds identified in the emissions profile in the Speciate 4.3 database, and to make such estimates for unspciated mixtures. The estimates will be highly uncertain for unspciated mixtures and also for some of the compounds, but use of upper and lower limits would allow the approximate magnitude of these uncertainties to be known. Therefore, we give upper and lower limit reactivity estimates as well as best estimates for each of the profiles, which would be quite different for profiles with unknown compositions or poorly studied compounds, and would be the same for profiles containing only compounds with known reactivity values. This is done for the MIR, MOIR, and EBIR scales, making a total of 9 scales with upper, lower, and best estimate reactivity values for each.

Approach

Tabulated Incremental Reactivities

The starting point in terms of reactivity values for this work were the MIR, MOIR, and EBIR reactivity values tabulated by Carter (2013b). These were calculated using the current version of the SAPRC-07 chemical mechanism as documented by Carter (2010a), with reactivity values for a number of compounds updated as described by Carter (2010b), with further updates and corrections made as indicated by Carter (2013b). The methodology used for calculating the reactivity values is essentially the same as employed previously (Carter, 1994, 2000a). The reactivity values are given in terms of grams ozone formed per gram VOC emitted, though it should be noted that the results should be used mainly in a relative sense since the actual grams of O₃ formed per gram VOC emitted would depend significantly on the conditions where it is emitted. The *ratios* of mass-based reactivity values would vary much less with scenario, especially if the scenarios have the same general types of NO_x conditions that was used to derive the general reactivity scale (Carter, 1994).

The reactivity values are given for a total of 1190 VOC compounds and mixtures. However, only the reactivity values for compounds or isomeric mixtures are used in this work, and a number of these compounds and mixtures are not used in the Speciate 4.3 chemical categories. Note also that these Speciate categories include compounds and mixtures whose reactivities are not given by Carter (2013b), so they had to be estimated for this work as discussed below.

Speciation Database Chemical Categories

The starting point of this work was emissions speciation database assignment database we developed for assigning model species used in the chemical mechanisms employed in current airshed models to the various chemical categories used in current speciation profile databases (Adelman et al, 2005; Carter, 2013a). For this purpose, we compiled a list of all the chemical categories used in the speciation profile databases, and categorized these as (1) individual chemical compounds; (2) simple isomeric mixtures of known individual compounds; (3) complex mixtures of known individual compounds and isomeric mixtures, (4) unknown or poorly characterized mixtures, and (5) compounds that have not been classified. The latter make negligible contributions to the mass in the profiles (no more than 0.8% in any profile, with an average of only 0.002%, and the amount of effort required to categorize them all was not judged to be worthwhile. Originally the database did not include Speciate 4.3 categories, but it has been updated to include all Speciate 4.3 categories except for some of those that are not used in any Speciate 4.3 profile.

The mixture categories whose compositions were known or could be estimated were assigned to the chemical compound categories, and additional chemical compound categories were added for this purpose if needed.

Assignments of model species used in various chemical mechanisms were made to as many of the individual chemical compound categories as possible. No assignments of model species were made directly to mixture categories; instead the assignments for mixtures were made based on model species assignments for the components of the mixtures. It has not been possible to make model species assignments for all the chemical compounds in the database because there is insufficient information about their atmospheric reactions that it is unknown which model species in the mechanisms are the best (or least bad) for them, and there were so many that it was not practical to estimate model species assignments for them all in an intelligent way in a reasonable amount of time. The procedure used was to sort the unassigned model species by their total mass fractions in all the profiles, and go through the list assigning them to model species in the various mechanisms to the compounds on the top of the list. Once we reached the point where the unassigned compounds accounted to no more than 0.002% on the average for the profiles, with no profile having more than 1% of such compounds, we decided that the point of diminishing returns was reached and the remainder of the unassigned compounds were not assigned.

Model species assignments were made for the condensed versions of the SAPRC-99 (Carter, 2000a,b) and SAPRC-07 (Carter, 2010a,c; Hutzell et al, 2012) mechanisms for airshed models, as well as other current mechanisms developed for such models such as CB05 (Sarwar et al, 2008) and RACM-2 (Goliff and Stockwell, 2013). All compounds were either completely assigned to all these condensed mechanisms or to none, in order to assure consistent processing of emissions for models with different mechanisms. Compounds for which no assignments are made for any mechanism are referred to as "unassigned compounds" in the subsequent discussion.

Reactivity Assignments to Compounds

All of the chemical categories identified as single compounds in the speciation database are listed in Table A-1 in the Appendix to this report². The reactivity assignments depend on the compound, as discussed below. The table includes a column with code numbers (1-4) indicating the type of assignments made for each compound.

² Appendix to this report consists of tables in an Excel spreadsheet document, Speciate-Reactivity-Appendix.xls, which is distributed along with this report. See the discussion of the Appendix at the end of this document.

Compounds with Known Reactivities

The MIR and other reactivity scales were calculated for the detailed version of SAPRC-07, which is different from the condensed versions of SAPRC-07 for airshed models assigned to the compound categories as discussed above. The model species in detailed SAPRC are referred to as "detailed model species" (DMS), and these are the species for which reactivity scales are calculated. Detailed model species for which reactivities were calculated were assigned for all compound categories that correspond to the compound being represented. These include not only those representing individual compounds explicitly, but those detailed model species representing isomeric mixtures of compounds assumed in the reactivity scale calculations to have the same mechanisms and therefore incremental reactivity. For example, the detailed model species "BR-C15" refers to all C₁₅ branched alkanes regardless of their structures, and all such compounds were assigned to this model species unless there was a different model species in the detailed SAPRC-07 mechanism that represented that compound explicitly. In that case, the compound was represented the model species that represented it explicitly.

For these compounds, which are designated using code number 1 on Table A-1, the best estimate reactivity value in the MIR, MOIR, and EBIR scales were taken as the value given in the spreadsheet given by Carter (2013b) for the detailed SAPRC-07 model species assigned to them. This value was also used for the upper limit and lower limit MIR, MOIR, and EBIR values, because there was no uncertainty in the assignments. Note that there are uncertainties in the mechanisms and reactivity calculation methods employed to derive the scales, but the upper and lower limit estimates in this work reflect only uncertainties in deriving the reactivity values from the values given by Carter (2013b).

Compounds Assigned Only to Lumped Model Species

There are a number of compounds in the database that have lumped model species assigned to them but that do not correspond to any detailed SAPRC-07 model species with reactivity values. Reactivity estimates for these compounds, which are designated using code number 2 in Table A-1, were derived based on the estimated upper, lower, and best estimate reactivity values assigned to the lumped model species or the type of compound. These were derived from the reactivity values for the compounds lumped with this model species or type of compound that have been detailed model species and therefore reactivity values.

Table A-2 in the Appendix lists the 18 lumped groups that were used for estimating reactivities for compounds not assigned detailed model species, and the averages, minimum, and maximum incremental reactivities of the various detailed model species in these groups. Note that amines were separated out from ALK5 and naphthalenes and polycyclic aromatics (PAH's) were separated out from ARO2 because they have different reactivity characteristics, despite not having separate lumped model species for them in lumped SAPRC-07. The incremental reactivities are given in molar units because it was assumed that compounds in the same group had similar reactivities on a molar basis, because that is what is determined by the mechanism for the compound.

The averages of the molar incremental reactivities of the compounds with known reactivities in the groups were taken as the best estimate reactivities of the compounds in the groups that had no reactivities otherwise assigned. The upper and lower limits were taken as the maximum and minimum molar incremental reactivities of these compounds. These were all converted to incremental reactivities on a mass basis based on the molecular weights of the compound and ozone³.

³ Incremental reactivity, mass basis = incremental reactivity, mole basis x molecular weight of ozone / molecular weight of the compound.

Unassigned Compounds

As discussed above, a number of compounds in the speciation database have not had detailed or lumped model species assigned to them because the assignments were difficult or arbitrary to make and collectively they represented only small fractions of the mass of the profiles. These are designated using code number 3 in Table A-1. For these compounds the lower limit incremental reactivities in all the scales were set at zero, and the upper limit reactivities in the MIR scale were assigned to the upper limit MIR (ULMIR) values derived as described by Carter (2010b). As discussed there, plots of MIRs of for all compounds in the SAPRC-07 MIR scale against molecular weight indicated that the following dependence of mass-based MIRs against molecular weight give a reasonable estimate of ULMIR's for estimation purposes:

$$\text{ULMIR} = \text{Min} \{ 20.19, 1.05 \times [(873.53 / \text{Mwt}) + (259.49 / \text{Mwt})^2] \},$$

where Mwt is the molecular weight in grams/mole, and the units of ULMIR are grams O₃ per gram VOC. For the MOIR and EBIR scales, the upper limit reactivity values were derived from the ULMIR value multiplied by the MOIR/MIR or EBIR/MIR ratios calculated for the mixture used to derive best estimate reactivities for unknown mixtures, as discussed below. These ratios are 0.42 for MOIR and 0.21 for EBIR (See Table A-4 in the Appendix). Note that these upper limits depend only on the molecular weight of the compound.

Best estimate reactivities for unassigned compounds were deriving from best estimate reactivities of components of the mixture derived as part of our speciation database for making model species assignments for compounds with unknown mechanisms (Carter, 2013a). This mixture was derived from the molecule-weighted average of compounds represented by SAPRC-99 mechanism (Carter, 2000a) in each SAPRC-99 chemical class. It was not updated for SAPRC-07, but is expected to be similar. The composition of this mixture, and the best estimate incremental reactivity values derived for it and its components, are given in Table A-3 in the Appendix.

Some Speciate 4.3 categories that refer to pure compounds were not assigned molecular weights or model species because making assignments for them were given low priority because of very low total contributions to the mass of the profiles. Since their molecular weights are not assigned, they could not be assigned upper limit reactivity values as described above. Such compounds were treated as mixtures of unknown compositions, and their reactivities were derived as discussed later in this report. Note that reactivity assignments for these categories have negligible impacts on reactivity assignments for the profiles because of their low mass contributions.

Non-Volatile Compounds

All compounds in the current speciation database (Carter, 2013a) with 20 or more carbons and some compounds with fewer carbons but with groups expected to result in low volatilities (e.g., acids) were judged not to have sufficient volatility to be available to react in the gas phase and form ozone. These compounds are designated using code number 4 on Table A-1. Such compounds were assigned upper, lower, and best estimate incremental reactivities of zero, since if compounds are not in the gas phase they will not react to form ozone. Note that the criteria we used to judge non-volatility is somewhat arbitrary and probably should be updated based on more comprehensive assessments of vapor pressures and partitioning properties for the various compounds. Such an assessment has been beyond the scope of our speciation database projects to date.

Reactivity Assignments for Mixtures

Table A-5 in the Appendix lists all the categories used to identify types of VOCs in the Speciate 4.3 database, gives ID's and molecular weights used in the Speciation Database, a code indicating the type of category, and the assigned reactivity values for the categories. The types include 1 for pure compound, whose reactivities were derived as discussed above, 2 for mixtures of known compounds, and 3 for mixtures whose compositions are unknown. Note that molecular weights for mixtures of known compounds can be derived based on the total number of moles in one gram of mixture⁴, but the molecular weights of mixtures of unknown composition are unknown. As discussed above, compounds that do not have assigned molecular weights or reactivities are also treated as unknown mixtures so are also given code number 3. The reactivity assignments for the two types of mixtures or for unassigned molecular weight categories were derived as discussed below.

Mixtures with Known Compositions

The mass-based reactivity values for mixtures of known composition were derived by the sum of the mass fraction of the components multiplied by their mass-based reactivity. The compositions of the mixtures are given in the speciation database spreadsheet that is available online (Carter, 2013a) and are not given here. These calculations were done separately for the best estimate, upper limit, and lower limit reactivities in the three scales. The results are given in Table A-5 in the appendix.

Note that if the mixture contains only compounds that have reactivity values given for them by Carter (2013b), then the best estimate and upper and lower limit reactivity values will be the same. The upper and lower limits do not reflect uncertainties in the compositions of the mixtures themselves, though in some cases these uncertainties are non-negligible. The upper and lower limits become more different for mixtures containing compounds that do not have reactivity values assigned but do have model species assignments, and most different if they contain compounds with no model species assignments.

Categories with Unknown Compositions or Unassigned Molecular Weights

Mixtures with unknown compositions and compounds with unassigned molecular weights were assigned lower limit reactivities of zero. Best estimate reactivities were assigned the mixture derived as part of our speciation database for making model species assignments for unknown mixtures (Carter, 2013a). This mixture was derived from all compounds with more than 6 carbons and molecular weight greater than 120 grams/mole for all compound in the Speciate 3.2 all profile average. It was not updated for Speciate 4.3, but is expected to be similar. The composition of this mixture, and the best estimate incremental reactivity values derived for it and its components, are given in Table A-4 in the Appendix. The best estimate MIR, MOIR, and EBIR values for this mixture was calculated to be 1.86, 0.79, and 0.38 grams O₃ per gram mixture, respectively. These were used for all categories of unknown compositions.

As discussed above, the upper limit incremental reactivity estimates for compounds depends on the molecular weight of the compound, which isn't known for mixtures of unknown composition. Therefore, the ULMIR and other upper limit reactivities were estimated based on the average molecular weight of the mixture used to represent unknown mixtures. As shown on Table A-4, the average molecular weight of this mixture (i.e., 1 / total moles in 1 gram), was 137.19 grams/mole. This gives upper limit MIR, MOIR, and EBIR values of 10.44, 4.41 and 2.16 grams O₃ /gram mixture, respectively. These were used for all categories of unknown compositions.

⁴ Molecular weight of mixture = 1 / moles in one gram of mixture = 1 / sum over components (weight fraction of component / molecular weight of component).

As indicated above, reactivity estimates for unknown mixtures were also applied to compounds whose molecular weights were not assigned. Strictly speaking molecular weights should be assigned for all compounds to give more refined upper limit reactivity estimates, but this was not done because of the relatively small contribution of such compounds to the total mass of any profiles compared to the level of effort required.

Some mixtures of unknown composition are judged to be nonvolatile based on the description of the mixture. These mixtures are given incremental reactivities of zero for all scales, as discussed above for compounds judged to be nonvolatile.

Reactivity estimates for profiles

The mass-based reactivity values for the VOC profiles in the Speciate 4.3 database were derived by the sum of the mass fraction of the Speciate 4.3 categories listed in Table A-5 multiplied by their mass-based reactivity as given in that table. The mass fractions of Speciate 4.3 categories for the profiles are given as part of the Speciate 4.3 database (EPA, 2012). The mass fractions do not sum up exactly to 100% for a small number of profiles, though this error was not large (the maximum was 101% and the minimum was 96%). Nevertheless, the fractions were normalized for all profiles so that mass was not under- or over-counted. These calculations were done separately for the best estimate, upper limit, and lower limit reactivities in the three scales.

Results and Discussion

Table A-6 in the Appendix lists all the profiles in the Speciate 4.3 database and the best estimate, maximum, and minimum incremental reactivity assignments for the MIR, MOIR, and EBIR reactivity scales. The mass fractions of unknown mixtures and of compounds with no mechanism assignments are also given on that table. These data can be used to assess the contributions of the various emissions sources to ozone formation in the various scales, with the upper and lower limit values indicating the magnitude of the uncertainties in these reactivity assignments, as discussed below. Note that the ozone impacts would also depend on the amount emitted from the source, which would vary significantly from source to source and depend on the region where the emissions are occurring. An example of use of these data for reactivity assessment of emissions inventories is given by Adelman et al (2013). Further discussion of the implications and use of these results with regard to the relative importances of different types of sources to ground-level ozone formation is beyond the scope of this report.

Note that the uncertainty ranges indicated by the upper and lower limit reactivity values reflect only the uncertainty in the chemical compositions of speciation categories used for the profiles and the uncertainty in estimating incremental reactivities of compounds for which incremental reactivity values have not been explicitly calculated. They do not incorporate uncertainties in the mechanisms or reactivity values calculated for the individual compounds listed by Carter (2010, 2013b), which can vary considerably from compound to compound depending on uncertainties in its mechanism and availability of data for mechanism evaluation. The reactivity tabulations given by Carter (2010, 20103) give codes giving subjective and qualitative indications of the uncertainties in the chemical mechanisms used to calculate the reactivities for the various compounds, and the availability of data to evaluate the capability of the mechanism used to accurately predict ozone formation. The uncertainty ranges also do not reflect uncertainties in compositions compounds that have been assigned to known mixture categories. A discussion of these uncertainties is beyond the scope of this work.

There is also uncertainty concerning which type of VOC reactivity scale is optimum for ranking VOC impacts for ozone control strategy purposes. The MIR scale is the most widely used for this purpose

but it may not be optimum for all regions and applications. See Hales (2007) and references cited therein for a discussion of work related to uncertainties in terms of the general reactivity assessment methodologies used for the MIR and other scales. Discussion of this is also beyond the scope of this work.

The uncertainty ranges also do not reflect the uncertainties in the profiles themselves, which are probably quite significant in some cases. A discussion of this is also beyond the scope of this project. However, since reactivity assignments have been made for all the chemical categories used in Speciate 4.3, it should be straightforward to update the reactivity assignments for profiles when their compositions are updated.

Appendix: Spreadsheet with Tables

Most of the tables referenced in this report are sufficiently large that they are more usefully presented in spreadsheets rather than as tables in the body of this report. These are given in an Excel file named Speciate-Reactivity-Appendix.xls that is distributed along with this report. This spreadsheet is available along with this report at the speciation database website (Carter, 2013a). The tables in this Appendix are given in separate sheets, and there is also a sheet listing the table numbers and captions. The data in the columns are described in the sheets themselves when not obvious, generally at the top or the bottom of the tables. The tables and captions are as follows:

- Table A-1. List of compounds in the speciation database, assigned SAPRC-07 detailed and lumped model species, and assigned incremental reactivity values.
- Table A-2. Summary of molar incremental reactivities various SAPRC-07 lumped groups
- Table A-3. Components of the mixture used to derive best estimate reactivities for compounds with no mechanisms assigned to them, and reactivity assignments for the mixture and components.
- Table A-4. Components of the mixture used to derive best estimate reactivities for unknown mixtures, and reactivity assignments for the mixture and components.
- Table A-5. List of VOC categories used in the Speciate 4.3 database and reactivity assignments for each.
- Table A-6. List of VOC speciation profiles in the Speciate 4.3 database and reactivity assignments for each.

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