ESTIMATION OF UPPER LIMIT
MAXIMUM INCREMENTAL REACTIVITIES OF VOCs

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July 16, 1997

Abstract

A procedure is presented for estimating upper limit Maximum Incremental ozone Reactivities (MIR's) for volatile organic compounds (VOCs) whose atmospheric ozone impacts are uncertain. This might be applicable for including compounds of unknown reactivity in reactivity-based regulations which employ the MIR scale for quantifying ozone impacts. The procedure is based on deriving upper limits for the two factors which determine the ozone impact of a compound in pollution episode: the fraction of emitted VOC which reacts during the episode (the kinetic reactivity), and the amount of ozone formed per molecule of VOC which reacts (the mechanistic reactivity). Upper limit kinetic reactivities are derived from the rate constants for the atmospheric reactions of the VOCs if they are known, otherwise a maximum kinetic reactivity of unity is assumed. Upper limit mechanistic reactivities are obtained from calculated relative mechanistic reactivities for a variety of VOCs for MIR scenarios, with lower upper limits being obtained for compounds known not to photolyze, or for alkanes or saturated compounds containing only alcohol, ether or ester groups. The information needed for making such estimates are discussed, and examples are given for representative VOCs whose reactivities are reasonably well known.

Introduction

In recognition of the fact that volatile organic compounds (VOCs) differ in their impacts on photochemical ozone formation, The California Air Resources Board (CARB) has implemented ozone reactivity adjustments in vehicle emissions regulations (CARB, 1993), and is now considering use or reactivity adjustments in regulations of VOCs from consumer products. The reactivity adjustments currently used in the CARB vehicle regulations are based on the Maximum Incremental Reactivity (MIR) scale (Carter, 1994a), and an updated version of this scale would likely be used in any consumer product reactivity-based regulations. Although ozone impacts of VOCs depend on atmospheric conditions (Carter and Atkinson; 1989; Carter, 1994a; Jeffries and Crouse, 1991), the MIR scale was chosen for this purpose because it reflects ozone impacts under conditions where ozone is most sensitive to VOC emissions, and because it has been shown to correlate reasonably well to effects of VOCs on integrated ozone and ozone exposure (Carter, 1994a; McNair et al 1992, 1994; CARB, 1993).

One problem with implementing reactivity adjustments in VOC regulations for consumer products and other stationary sources is that a wide variety of VOCs are involved, including many whose ozone impacts are highly uncertain or unknown. Some means is necessary to incorporate such compounds in reactivity-based regulations which provides incentives for using compounds of known low reactivity, but which is not unduly burdensome to the producers and users of compounds of unknown reactivity, some

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of which may also turn out to be beneficial. One approach is to use "default" reactivity factors for compounds whose reactivities are unknown, which would be the upper limit of their actual likely ozone impact. This approach allows regulations to cover compounds of both known and unknown reactivity in a relatively simple and consistent manner, and provides incentives for producers or users to reduce the uncertainties concerning the environmental effects of the emissions they cause. For this approach to be acceptable, the default reactivity factors must not be so high that they cause an unfair burden to producers and users of new or unstudied compounds, which may turn out to have relatively low reactivity. Ideally, they should incorporate, to the maximum extent possible, any knowledge we have concerning the likely upper limit ozone impacts of the compounds, so they will not be higher than absolutely necessary given the limitations in our knowledge. In addition, the procedures for deriving them should not be so complex that they cannot be applied to large numbers of unstudied compounds that might be covered by reactivity-based regulations.

Given below is a suggested set of procedures which can be employed to estimate upper limit MIR's for VOCs for which limited kinetic or mechanistic information is available. The procedures take into account our current knowledge concerning the general factors which affect ozone reactivities of all VOCs, providing a means for appropriate upper limit values to be derived for compounds whose atmospheric reaction rate constants are known, or which belongs to classes of compounds where the range of possible oxidation products and mechanisms are reasonably well understood.

Factors Affecting Reactivity
Kinetic and Mechanistic Reactivities

For regulatory applications, the appropriate quantification of ozone impact is the *incremental reactivity*, which is the amount of additional ozone formation caused by adding a small amount of the compound to the emissions, divided by the amount emitted (Carter and Atkinson, 1989; Carter, 1994a). For upper limit estimation purposes, it is useful to think of incremental reactivities as being a product of three factors, as follows (Carter and Atkinson, 1989):

$$\text{Incremental Reactivity (Ozone per mass VOC emitted)} = \text{Kinetic Reactivity (VOC reacted /VOC emitted)} \cdot \text{Mechanistic Reactivity (moles } O_3 \text{ /mole VOC reacted)} \cdot \text{Mass Conversion Factor (moles VOC /mass VOC)} \tag{1}$$

The *kinetic reactivity* is the fraction of the emitted VOC which undergoes chemical reaction in the atmosphere during the time period being considered. It depends primarily on the rate constants for the VOCs atmospheric reactions, but also on the overall levels of OH radicals, ozone, or light in the scenario, depending on how the VOC reacts. Being a fraction, it is a unitless number. Note that kinetic reactivity is *not* the same as the atmospheric reaction rate, which is the speed at which it reacts. Although they are approximately proportional for slowly reacting compounds, for rapidly reacting compounds the kinetic reactivity is approximately unity, and thus almost independent of the reaction rate. Therefore, if insufficient information is available to derive upper limit atmospherically relevant rate constants for a compound, then kinetic reactivities of unity can be used for upper limit estimation purposes.

The *mechanistic reactivity* is the number of molecules of ozone formed for each molecule of VOC which reacts. It reflects both the nature of the VOCs reaction mechanism and also the efficiency of ozone formation from the reactions of VOCs in the particular scenario. Although the mechanistic reactivities factor can be given in other units besides molecules ozone per molecule VOC, molecular units are more

meaningful chemically and therefore are more straightforward to use for estimation purposes. Upper limits for mechanistic reactivities can be estimated based on the range of mechanistic reactivities of compounds with known mechanisms or ozone impacts, as discussed below. In some cases, structural information and knowledge of the general features of atmospheric chemistry may permit limiting the range of possible mechanisms and products, allowing for lower upper limit estimates for mechanistic reactivities for certain types of compounds.

The product of the kinetic and mechanistic reactivities are incremental reactivities in units of molecules of ozone formed per molecule of VOC emitted. Since emissions of VOCs are quantified and regulated on a mass basis, the appropriate incremental reactivity units for regulatory applications is ozone formed per unit mass of VOC emitted. Therefore, a *mass conversion factor* is applied to place the incremental reactivities on a mass VOC basis. It is inversely proportional to the VOC's molecular weight.

Environmental Conditions

Both kinetic and mechanistic reactivities depend on the conditions of the environment where the VOC reacts. For example, the OH radical levels in the environment determine the fraction reacted for a VOC which reacts primarily with OH radicals, and the NO_x levels significantly affect the efficiency for O_3 formation once a VOC reacts, which determines its mechanistic reactivity (see, for example, Carter and Atkinson, 1989). However, if the VOCs with known reactivities are to be regulated according to their MIR's, then we need only be concerned with estimates of kinetic and mechanistic reactivities for MIR conditions. Therefore, in this work we are concerned only with a single set of environmental conditions, which is that used to derive the MIR scale.

MIR conditions consist of scenarios where the NO_x inputs have been adjusted so that the peak ozone levels are the most sensitive to changes in total reactive VOC emissions. The MIR scale developed by Carter (1994a) is based on averages of incremental reactivities calculated for 39 different single-day EKMA model scenarios (Baugues, 1990) where NO_x inputs have been adjusted in this way. However, it was also found that incremental reactivities calculated using a single "Averaged Conditions" MIR scenario were essentially the same, to within a few percent for all positively reactive VOCs, as average reactivities calculated from the 39 MIR scenarios. Therefore, for the purpose of estimating approximate upper limit kinetic and mechanistic reactivities for upper limit MIR determinations, it is sufficient to limit our consideration to the Averaged Conditions MIR scenario. The detailed input data and derivation of this scenario are given elsewhere (Carter, 1994a,b).

Upper Limit Kinetic Reactivities for MIR

Information Required

Most VOCs react in the atmosphere with OH radicals, and many also react to non-negligible extents with O_3, NO_3 radicals, or by photolysis, If insufficient information is available concerning the rate constants for these processes (or their upper limits) under atmospheric conditions, then an upper limit kinetic reactivity of unity should used when deriving upper limit MIR values. However, for many if not most VOCs, sufficient information is available to permit more precise kinetic reactivity estimates. The minimum information for making kinetic reactivity estimates are summarized in the following section.

OH Radical Rate Constant. Because VOCs react in the atmosphere with OH radicals, the rate constant for this reaction, or its upper limit, must be determined, or its upper limit must be estimated. Some VOCs can be concluded not to react significantly with OH radicals based on the lack of modes for which OH to react, such as abstractable hydrogens or double bonds. Only if a VOC contains only functional groups which have been shown in other molecules not to react with OH radicals, or if there are

no thermodynamically feasible means for OH radicals to react with the compound, it is safe to conclude that it does not react with OH radicals without the benefit of carrying out a direct experimental measurement. (Because of possible interactions, functional groups which are immediately adjacent to another functional group should be considered to be different from those which are isolated. This is applicable for all reactions discussed here.) Available information concerning OH + VOC rate constants is summarized by Atkinson (1989, 1994).

Methods exist for estimating OH radical rate constants for many compounds which are usually accurate to within a factor of 2 or better (Kwok and Atkinson, 1995). Therefore, if no measurements are available concerning the OH radical rate constant of the compound, but the rate constant can be measured using the methods of Kwok and Atkinson (1995), then a rate constant which is two times the estimated value can be used for the purpose of making upper limit kinetic reactivity estimates. The factor of two increase is necessary to take into account the uncertainty of the estimation methods when making upper limit determinations.

Ozone Rate Constant. Some VOCs, usually (but not always) those with C=C double bonds, can react with ozone at significant rates, and these reactions often have a net positive effect on ozone because of the subsequent reactions of the radicals formed. Only if a VOC contains only functional groups which have been shown in other molecules not to react with ozone, or if there are no thermodynamically feasible means for such a reaction to occur, is it safe to conclude that the reaction with ozone will be negligible in the absence of direct experimental measurement. Available information concerning ozone + VOC rate constants is given by Atkinson and Carter (1984), and is updated by Atkinson (1994).

Although Atkinson and Carter (1984) discuss possible approaches for estimating O_3 rate constants, no comprehensive approach has been developed which performs very reliably for estimation purposes. Therefore, if the compound contains groups which might possibly react with O_3 (e.g. C=C, C=N, or N-N bonds), and its O_3 rate constant has not been measured or its upper limit determined, then a kinetic reactivity of unity must be assumed when making upper limit reactivity estimates.

NO_3 Radical Rate Constant. Some VOCs, usually (but not always) those with C=C double bonds, can react with NO_3 radicals at sufficiently high rates to affect their ozone impact. Only if a VOC contains only functional groups which have been shown in other molecules not to react with NO_3 radicals, or if there are no thermodynamically feasible means for such a reaction to occur, is it safe to conclude that this reaction with ozone will be negligible in the absence of direct experimental measurement. Available information concerning NO_3 + VOC rate constants is given by Atkinson (1991, 1994). Atkinson (1991, 1994) also gives methods for estimating these rate constants. As with the OH radical rate constant, if the rate constant has to be estimated, then the estimate should be increased by a factor of two for upper limit reactivity estimates.

Photolysis Rates. Some VOCs can react in the atmosphere by direct photolysis, and if photodecomposition is sufficiently rapid and involves radical formation, then it can result in high ozone impacts for the VOC. Upper limit atmospheric photolysis rates can be estimated given the compound's UV-visible absorption spectrum for wavelengths $\geq$ 290 nm, and the actinic fluxes for direct overhead sunlight for clear-sky conditions, assuming unit quantum yields. The actinic fluxes given by Peterson (1976) should be sufficient for this purpose. Only if the VOC contains only functional groups which have no absorption at $\lambda \geq$ 290 nm, or has no decomposition pathway with a heat of reaction of less than the energy of a 290 nm photon, is it safe to conclude that the compound will not photolyze in the absence of absorption cross section data. If the compound has non-negligible absorption cross sections in the λ

$\geq$ 290 nm region, then unit quantum yields should be assumed for making upper limit photolysis rate estimates, unless there is information justifying the use of lower quantum yields for this purpose. Information concerning absorption cross sections and quantum yields for photolyses of smaller molecules of atmospheric significance are given in the most recent NASA (1994) and IUPAC (Atkinson et al, 1997) evaluations, though for higher molecular weight VOCs, and organics in general, there does not appear to be a more current or comprehensive review of absorption cross section data than that of Calvert and Pitts (1966).

Estimation of MIR Kinetic Reactivities from Rate Constants

Most VOCs react significantly only with OH radicals. In this case, the fraction reacted in given scenario can be estimated by

$$\text{Kinetic Reactivity} \approx (1 - e^{-kOH \cdot EffIntOH})$$
$$\approx kOH \cdot EffIntOH \quad \text{(if } kOH \cdot IntOH <<1) \qquad (3)$$

where kOH is the VOC's OH radical rate constant, and EffIntOH is a scenario-dependent "Effective Integrated OH" parameter which is related to, but is not exactly the same as, the integrated OH radical levels (Carter and Atkinson, 1989). Note that for slowly reacting compounds, Equation (3) predicts that the kinetic reactivities are approximately proportional to the integrated reaction rates, while for rapidly reacting compounds the kinetic reactivity approaches the upper limit value of unity. For the Averaged Conditions MIR scenario, a value of

$$EffIntOH^{MIR} = 1.6 \text{ x } 10^{11} \text{ molec cm}^3 \text{ s}$$

is appropriate for use in upper limit kinetic reactivity estimates. This gives good fits to kinetic reactivities for VOCs with kOH $< 5 \text{ x } 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, while slightly overestimating (by no more than ~5%) kinetic reactivities for faster reacting compounds.

Equation (3) obviously will not work if the VOC reacts significantly with O_3 or NO_3 radicals or undergoes photolysis. For the purpose of estimating kinetic reactivities for such compounds, we assume that Equation (3) can be generalized to

$$\text{Kinetic Reactivity} \approx (1 - e^{-\text{Integrated Reaction Rate}}) \qquad (4)$$

where

$$\begin{matrix} \text{Integrated Reaction} \\ \text{Rate} \end{matrix} \approx kOH^{VOC} \cdot IntOH + kO_3^{VOC} \cdot IntO_3 + kNO_3^{VOC} \cdot IntNO_3 + \int kPhot^{VOC}dt \qquad (5)$$

and IntOH, $IntO_3$, and $IntNO_3$ are the integrated levels of OH radicals, O_3, and NO_3 radicals, respectively, and $\int kPhot^{VOC}dt$ is the integrated photolysis rate. (Note that IntOH, the actual integrated OH radical levels, is not the same as EffIntOH, which depends on the when the VOC is emitted in the scenario as well as the integrated OH radical levels.) For the Averaged Conditions MIR scenario, the integrated OH, O_3, and NO_3 are

$$IntOH^{MIR} = 1.9 \text{ x } 10^{11} \text{ molec cm}^{-3} \text{ s}$$
$$IntO_3^{MIR} = 8.5 \text{ x } 10^{16} \text{ molec cm}^{-3} \text{ s, and}$$
$$IntNO_3^{MIR} = 7.3 \text{ x } 10^{11} \text{ molec cm}^{-3} \text{ s.}$$

An estimate of the upper limit $\int kPhot^{VOC}dt$ can be obtained using the measured cross sections, the measured or upper limit quantum yields, and the clear-sky, direct overhead sun actinic flux data (such as those given by Peterson, 1976) to calculate the maximum photolysis rate, $kPhot^{VOC}_{max}$. If there is no information available concerning the quantum yield for the photodecomposition of the compound (as usually is the case), then unit quantum yields at all wavelengths should be assumed. For the Averaged Conditions MIR scenario, the integrated photolysis rate can then be approximated from $kPhot^{VOC}_{max}$ using:

$$\int kPhot^{VOC}dt \approx 3.6 \text{ x } 10^4 \text{ s} \cdot 0.7 \cdot kPhot^{VOC}_{max} \approx 2.5\text{x}10^4 \text{ sec} \cdot kPhot^{VOC}_{max} \tag{6}$$

where $3.6 \text{ x } 10^4$ seconds is the length of time in the scenario [10 hours for all EKMA scenarios used by Carter (1994a,b)], and the 0.7 factor is the ratio of the average to the maximum photolysis rate, and was derived for the photolysis of NO_2 in the Averaged Conditions MIR scenario. Most photolysis reactions are more sensitive to shorter wavelength UV than is NO_2 photolysis, and would have a lower average-to-maximum ratio because their photolysis rates would vary more with solar zenith angle. Therefore, the 0.7 factor is considered appropriate for upper limit estimates. To be consistent with the units shown above, the units of $kPhot^{VOC}_{max}$ should be s^{-1}.

Equations (4) and (5) can be combined to yield

$$\text{Kinetic Reactivity} \approx (1 - e^{-\text{Effective kOH} \cdot \text{EffIntOH}}) \tag{7}$$

where

$$\text{Effective kOH}^{VOC} = kOH^{VOC} + \frac{IntO_3}{IntOH} \text{ } kO_3^{VOC} + \frac{IntNO_3}{IntOH} kNO_3^{VOC} + \frac{3.0\text{x}10^4}{IntOH} kPhot^{VOC}_{max}$$

Using the $IntOH$, $IntO_3$, $IntNO_3$, and $\int kPhot^{VOC}dt/kPhot^{VOC}_{max}$ for the Averaged Conditions MIR scenario (see above), we then obtain

$$\text{Effective kOH}^{VOC} \approx kOHVOC + 5\text{x}10^5 \text{ } kO_3^{VOC} + 4 \text{ } kNO_3^{VOC} + 1.3\text{x}10^{-7} \text{ } kPhot^{VOC}_{max}. \tag{8}$$

where the units of the bimolecular rate constants are $cm^3 \text{ molec}^{-1} \text{ s}^{-1}$, and the units of $kPhot^{VOC}_{max}$ is s^{-1}. This in effect amounts to a correction to the OH radical rate constant for the other reaction pathways for the purpose of estimating kinetic reactivities.

Table 1 gives the rate constants and the corresponding estimated MIR kinetic reactivities for a number of representative VOCs. To allow for comparisons with directly calculated (i.e., best estimate) MIR data, Table 1 only shows those VOCs whose mechanisms are sufficiently well established for direct MIR calculations. The kinetic reactivities calculated directly for the Averaged Conditions MIR scenario are also shown on the table. It can be seen that Equation (8) gives good predictions of the directly calculated values. To allow for more straightforward comparisons for photolysis reactions, the $kPhot^{MAX}$ values on Table 1 were calculated using the quantum yields in the model. However the quantum yields would not be known for most photoreactive VOCs for which upper limit reactivity estimates have to be made, and thus unit quantum yields, giving higher $kPhot^{MAX}$ values and therefore higher kinetic reactivities, would be used.

Estimation of Upper Limit MIR Maximum Mechanistic Reactivities

Upper limit estimates for mechanistic reactivities can be obtained from examining the mechanistic reactivities for a sufficiently wide variety of VOCs under MIR conditions. The updated (Carter, 1995; Carter et al, 1997a) version of the Carter (1990) detailed mechanism now contains separate representations for the atmospheric reactions of over 250 different types of VOCs, though only a fraction of these have been experimentally evaluated, and less than half are documented. To provide additional examples of compounds with high mechanistic reactivities, the reactions of chloropicrin (CCl_3NO_2) (Carter et al, 1997b) and methyl nitrite (CH_3ONO) (Unpublished results from this laboratory) have been added. Although some of these mechanisms are uncertain, they can be considered to represent a sufficiently wide variety of ways that VOCs can react for the purpose of establishing upper limit mechanistic reactivity estimates.

Figures 1 and 2 show the mechanistic reactivities for the Averaged Conditions MIR scenario calculated for a variety of VOCs. Note that the chemical mechanism used is the current updated version of the SAPRC mechanism (Carter et al, 1997a), so the mechanistic reactivities shown will be different than those calculated by Carter (1994a), who used the SAPRC-90 (Carter, 1990) mechanism. Figure 1 shows the mechanistic reactivities in units of moles O_3 per mole VOC reacted, and Figure 2 shows the values as moles O_3 per mole carbon reacted. The highest molar MIR mechanistic reactivities is in the ~30-35 range, which is observed for 1,3,5- and 1,2,3-trimethyl benzene, m-xylene, and biacetyl. The highest per-carbon MIR mechanistic reactivities are for methyl nitrite, biacetyl, and methyl glyoxal, which are in the range of ~7-11. However, if photoreactive compounds are excluded, then no compound has per-carbon MIR mechanistic reactivities which are significantly greater than ~4, which is observed for methane and a variety of olefins and aromatics.

These data suggest that the upper limit per molecule MIR mechanistic reactivities can be estimated by
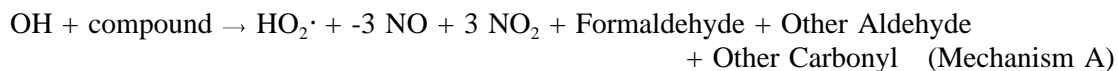
$$\text{Mechanistic Reactivity} \leq \text{MIN}(4 \cdot n_C, \ 35) \qquad (9)$$

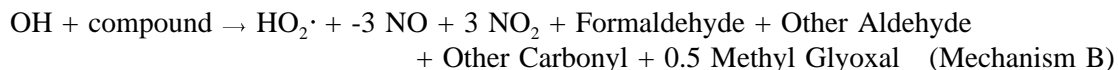for compounds which are known to be non-photoreactive, and by

$$\text{Mechanistic Reactivity} \leq \text{MIN}(11 \cdot n_C, \ 35) \qquad (10)$$

for photoreactive compounds or compounds for which photodecomposition cannot be ruled out. The units are moles of ozone per mole carbon VOC which reacts, and n_C is the number of carbons in the molecule.

For some compounds, specifically saturated hydrocarbons or non-photoreactive compounds containing only alcohol, ether, or ester groups, our knowledge of atmospheric reaction mechanisms, and how various types of reactions affects reactivity, can permit somewhat lower upper limit estimates to be made. Compounds such as these will react significantly only with OH radicals, would probably convert no more than 3-4 molecules of NO to NO_2, and the most reactive products they are likely to form are higher aldehydes or, in the case of esters, possibly some α-dicarbonyls such as methyl glyoxal (see, for example, Carter et al, 1993, 1996a-c, 1997c-e). Probably the most reactive reasonable mechanism for such compounds would be:

$$\text{OH} + \text{compound} \rightarrow \text{HO}_2\cdot + \text{-3 NO} + 3\text{ NO}_2 + \text{Formaldehyde} + \text{Other Aldehyde}$$
$$+ \text{Other Carbonyl} \quad \text{(Mechanism A)}$$

if the compound did not have a carbonyl group (i.e., not an ester), or

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$$\text{OH} + \text{compound} \rightarrow \text{HO}_2\cdot + \text{-3 NO} + \text{3 NO}_2 + \text{Formaldehyde} + \text{Other Aldehyde}$$
$$+ \text{Other Carbonyl} + \text{0.5 Methyl Glyoxal} \quad \text{(Mechanism B)}$$

otherwise. These are based on the observations that mechanisms with more than three NO to NO_2 conversions have not been observed for such compounds, aldehydes are the most reactive products expected to be formed from compounds not containing carbonyl groups but formation of more than two moles of aldehydes rarely occurs, and that although some carbonyl-containing compounds may form α-dicarbonyls (e.g., see Carter et al, 1997d), it is probably not the dominant reaction route since carbonyl substitution tends to deactivate OH reaction at groups next to it (Kwok and Atkinson, 1995).

As discussed by Carter and Atkinson (1989), mechanistic reactivities of compounds which react only with OH radicals can be expressed in terms of sums of mechanistic reactivities of "pure mechanism species", which reflect specific aspects of the VOC's mechanism, such as the numbers of NO to NO_2 conversions, and yields of various types of reactive products. Table 2 gives MIR mechanistic reactivities calculated for the major pure mechanism species likely to be involved in atmospheric reaction mechanisms of saturated hydrocarbons, alcohols, ethers or esters, and the corresponding mechanistic reactivities calculated for Mechanisms A and B, above. Note that the high mechanistic reactivities of the α-dicarbonyls make it appropriate to consider upper-limit reactivity mechanisms of carbonyl-containing compounds, whose reactions might result in formation of α-dicarbonyls, separately from upper limit mechanisms for compounds where these products cannot be formed.

Table 2 shows that mechanistic reactivities of some of the pure model species, and thus of the upper limit mechanisms A and B, are not completely independent of the OH radical rate constant, particularly at higher rate constants. In particular, although the mechanistic reactivity contribution of NO to NO_2 conversions is relatively unaffected by the reaction rate, the mechanistic reactivity contribution of reactive products tends to increase as the rate constant increases. For Mechanisms A and B, the Averaged Conditions MIR mechanistic reactivities shown on Table 2 can be fit by the following empirical equations:

$$\text{MIR Mechanistic Reactivity A} = 19.5 - 8.9 \exp(-3.9 \times 10^{10} \cdot \text{kOH}) \quad (11)$$
$$\text{MIR Mechanistic Reactivity B} = 28.5 - 14.5 \exp(-2.7 \times 10^{10} \cdot \text{kOH}) \quad (12)$$

where the units of the mechanistic reactivities are mole O_3 per mole VOC, and the kOH is the OH radical rate constants in units of cm^3 $molec^{-1}$ s^{-1}.

Based on these considerations, we conclude that for alkanes or saturated compounds containing no groups other than alcohols and ethers, and no atoms other than H, C, or O, then the upper limit mechanistic reactivity can be given by either Equation (9) or (11), whichever gives the lower value. Likewise, if the compound contains a carbonyl group but no other groups besides alcohol or ether and no atoms other than N, C, or O, then the upper limit mechanistic reactivity can be given by either Equation (9) or (12), whichever is lower. For any other compound, only Equations (9) or (10) can be used, depending on whether the compound is or may be photoreactive.

Table 1 gives the upper limit MIR mechanistic reactivities for the representative compounds whose MIR's have been calculated, and compares them with the mechanistic reactivities calculated using their best estimate mechanisms. The "MR Type" column on the table shows how the compounds were classified for the purpose of estimating upper limit mechanistic reactivities, and shows how the upper limit values were obtained. The upper limits are close to the directly calculated values for the most mechanistically reactive compounds such as methane some of the alkyl benzenes, but are up to a factor

of ~5-10 for compounds with low mechanistic reactivity such as naphthalenes or high molecular weight esters, where the relatively low upper limit mechanism A cannot be used. On the average, the upper limit mechanistic reactivities are higher than the directly calculated values a factor of ~3. Given the large variability and many factors that affect mechanistic reactivities, this is probably as close an estimate that can reasonably be obtained.

Upper Limit MIR Values

The upper limit kinetic and mechanistic reactivities derived as discussed above can then be combined, according to Equation (1) to obtain an estimate of the *incremental reactivity* in the MIR scale, which is the quantity of interest. The incremental reactivities obtained by multiplying the kinetic and mechanistic reactivities derived as discussed above will be in units of moles of ozone formed per mole VOC emitted, but for regulatory applications the appropriate units are grams of O_3 per gram VOC. This conversion is done by multiplying by the ratio of the molecular weight of O_3 to the molecular weight of the VOC. Therefore,

$$\begin{array}{cc} \text{Upper Limit MIR} \\ \text{(gm } O_3 \text{ / gm VOC)} \end{array} = \begin{array}{c} \text{Upper Limit} \\ \text{Kinetic Reactivity} \end{array} \cdot \begin{array}{c} \text{Upper Limit Mechanistic} \\ \text{Reactivity (mol } O_3 \text{ / mol VOC)} \end{array} \cdot \frac{48 \text{ (gm } O_3 \text{/ mol } O_3)}{\text{Mwt}^{\text{VOC}} \text{ (gm/mol)}}$$

(13)

The upper limit MIR's which were derived from the upper limit kinetic and mechanistic reactivities are shown on Table 1, where they can be compared with the best estimate MIR's which were directly calculated for the compounds using their current best estimate mechanisms[1].

Table 1 also shows the ratio of the upper limit to the calculated MIRs, which is in effect the margin of error involved in making the upper limit estimates. For these compounds, whose rate constants are reasonably well known, the difference between upper limit and best estimate MIRs reflect entirely the differences for the mechanistic reactivities. Obviously the differences between upper limit and best estimate would be greater if the rate constants were unknown or significantly uncertain, and unit kinetic reactivities had to be used.

Discussion

The recommendations for estimating upper limit reactivities were developed to assist the application of reactivity-based regulations to compounds of uncertain reactivity. The objective to derive upper limit MIR estimates for compounds of uncertain reactivity such that it is unlikely that the actual ozone impacts of the compounds would be higher than the upper limit, but which are as low as possible given our limited knowledge. It is also important that the procedure be as objective and straightforward as possible, so that it can be applied to the full variety of compounds which might be subject to reactivity based regulations. The procedures discussed above should adequately addresses these objectives.

The recommendations given in this work are based on reactivity calculations for a wide variety of compounds. However, it should be pointed out that the upper limit mechanistic reactivities for compounds with unknown mechanisms are driven primarily by calculated reactivities for aromatic hydrocarbons, methyl glyoxal, methyl nitrite, and methane. The other classes of compounds which were

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[1] Note that the best estimate MIR's on Table 1 are different than those given by Carter (1994) because of updates to the mechanism. The updates caused the MIR's to increase for most compounds, except for some compounds where new data indicate that the actual reactivities are less than previously estimated.

considered were primarily alkanes, olefins, and various relatively low molecular weight oxygenates (see Carter, 1990). If a compound is expected to possibly have a significantly different mechanism than any compound in this group, then the possibility that the ozone impacts may actually be higher than estimated using these procedures cannot be totally ruled out. In this case, the upper limit estimates would need to be modified accordingly. However, given our current knowledge of atmospheric chemistry and the variety of compounds studied, we think that the probability of any given compound having a greater ozone impact the upper limit estimate is relatively low.

It is important to recognize the limitations of this work. The procedure is intended only for estimating upper limits for Maximum Incremental Reactivities calculated using the approach and one-day EKMA model airshed scenarios employed by Carter (1990), and using the current version of the SAPRC mechanisms as described by Carter et al (1997a). The upper limit mechanistic reactivities are particularly sensitive to the type of scenario employed, and are also subject to change as the chemical mechanism is updated. Therefore, these upper limit estimates should not be considered as independent of the reactivity scale upon which it is based, but rather as an extension of it, which would be updated and modified as the scale is updated in the process of ongoing research.

In particular, the upper limits given here are *not* to be compared with MIR values used in the current CARB vehicle regulations (CARB, 1993), or those given by Carter (1994a), since they were calculated using an earlier chemical mechanism, which generally gives lower MIR values. Furthermore, they may also not be compatible with the updated MIR values being developed for the CARB, since the chemical mechanisms updates are still underway, and further changes are expected. The upper limit MIRs given on Table 1 should be compared *only* with the best estimate MIRs given on the same table, and not with those given in any previously published or distributed tabulation, or with any updated scale that may be developed in the future. However, the general approach discussed here can be used to update the upper limit estimates if any changes are made to the chemical mechanism or scenarios used to derive the underlying reactivity scale upon which this is based.

It is also important to recognize that the general procedures discussed here are only applicable to regulatory or other applications where, by their nature, the ozone impacts must be quantified using a single scale. Examples would include the CARB clean-fuel/low emissions vehicle regulations (CARB, 1993), or the reactivity adjustments to VOC content limits being considered for CARB consumer product regulations. This procedure is *not* applicable to applications such as deciding whether to exempt a VOC from regulation on the basis of having negligible ozone impact, which can be based on a VOC's impact under a full variety of atmospheric conditions. A set of procedures considered more appropriate for upper limit reactivity estimates for making VOC exemption decisions is described in a separate document (Carter, 1997).

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Table 1. Summary of rate constants, and directly calculated and upper limit estimates of kinetic, mechanistic, and incremental reactivities in the MIR scale for selected VOCs [a].

Compound or Mixture	Rate Constants (cm^3 $molec^{-1}$ s^{-1})				kPhot Max (s^{-1})	MR Type [b]	Upper Limit Estimate [c,d]			Direct Calculation [c,e]			Upper Limit / Direct
	Eff. kOH	kOH	kO_3	kNO_3			KR	MR (mol/mol)	MIR (gm/gm)	KR	MR (mol/mol)	MIR (gm/gm)	
Carbon Monoxide	2.4e-13	2.4e-13				A	0.038	4.0	0.26	0.039	1.0	0.06	4
Methane	8.7e-15	8.7e-15				A	0.0014	4.0	0.02	0.0014	4.0	0.02	1.0
Ethane	2.7e-13	2.7e-13				A	0.043	8.0	0.55	0.044	4.5	0.32	2
Propane	1.2e-12	1.2e-12				A	0.17	11.0	2.0	0.17	3.2	0.6	3
n-Butane	2.6e-12	2.6e-12				A	0.34	11.4	3.2	0.34	4.8	1.3	2
n-Octane	8.8e-12	8.8e-12				A	0.75	13.2	4.2	0.74	2.9	0.9	5
2,2,4-Trimethyl Pentane	3.7e-12	3.7e-12				A	0.45	11.8	2.2	0.45	6.5	1.2	2
Ethene	8.4e-12	8.4e-12	1.7e-18	2.2e-16		NP	0.74	8.0	10.1	0.73	6.8	8.4	1.2
Propene	2.6e-11	2.6e-11	1.1e-17	9.7e-15		NP	0.98	12.0	13.5	0.96	10.2	11.1	1.2
1-Butene	3.1e-11	3.1e-11	1.0e-17	1.2e-14		NP	0.99	16.0	13.6	0.97	12.9	10.7	1.3
1-Hexene	3.7e-11	3.7e-11	1.1e-17	1.2e-14		NP	1.00	24.0	13.6	0.98	10.3	5.7	2
Isobutene	5.2e-11	5.1e-11	1.2e-17	3.3e-13		NP	1.00	16.0	13.7	0.98	6.9	5.8	2
2-Methyl-1-Butene	6.1e-11	6.0e-11	1.2e-17	3.3e-13		NP	1.00	20.0	13.7	0.98	8.0	5.4	3
trans-2-Butene	6.5e-11	6.3e-11	1.9e-16	3.9e-13		NP	1.00	16.0	13.7	0.98	15.8	13.3	1.0
Isoprene	1.0e-10	1.0e-10	1.3e-17	6.9e-13		NP	1.00	20.0	14.1	1.00	13.4	9.4	1.5
a-Pinene	7.8e-11	5.3e-11	8.8e-17	6.1e-12		NP	1.00	35.0	12.3	0.98	11.2	3.9	3
b-Pinene	8.8e-11	7.8e-11	1.6e-17	2.5e-12		NP	1.00	35.0	12.3	0.99	5.5	1.9	6
d-Limonene	2.2e-10	1.7e-10	2.1e-16	1.2e-11		NP	1.00	35.0	12.3	1.00	8.3	2.9	4
Benzene	1.3e-12	1.3e-12				NP	0.19	24.0	2.7	0.19	6.9	0.8	3
Toluene	5.9e-12	5.9e-12				NP	0.61	28.0	8.9	0.61	16.4	5.2	2
Ethyl Benzene	7.1e-12	7.1e-12				NP	0.68	32.0	9.8	0.67	7.5	2.3	4
o-Xylene	1.4e-11	1.4e-11				NP	0.89	32.0	12.8	0.86	22.0	8.5	2
p-Xylene	1.4e-11	1.4e-11				NP	0.90	32.0	13.0	0.87	7.4	2.9	4
m-Xylene	2.4e-11	2.4e-11				NP	0.98	32.0	14.1	0.95	33.6	14.3	1.0
1,3,5-Trimethyl Benzene	5.7e-11	5.7e-11				NP	1.00	35.0	14.0	0.98	35.3	13.9	1.0
1,2,3-Trimethyl Benzene	3.3e-11	3.3e-11				NP	0.99	35.0	13.9	0.97	32.1	12.5	1.1
1,2,4-Trimethyl Benzene	3.2e-11	3.2e-11				NP	0.99	35.0	13.9	0.97	13.9	5.4	3
Tetralin	3.4e-11	3.4e-11				NP	1.00	35.0	12.7	0.97	3.0	1.1	12
Naphthalene	2.2e-11	2.2e-11				NP	0.97	35.0	12.7	0.93	3.6	1.3	10
2,3-Dimethyl Naphth.	7.7e-11	7.7e-11				NP	1.00	35.0	10.8	0.99	16.2	4.9	2
Alkyl Phenols	1.3e-10	4.2e-11		2.1e-11		NP	1.00	28.0	12.4	1.00	5.8	2.6	5

Compound or Mixture	Rate Constants (cm^3 molec^{-1} s^{-1})				kPhot Max (s^{-1})	MR Type [b]	Upper Limit Estimate [c,d]			Direct Calculation [c,e]			Upper Limit / Direct
	Eff. kOH	kOH	kO$_3$	kNO$_3$			KR	MR (mol/mol)	MIR (gm/gm)	KR	MR (mol/mol)	MIR (gm/gm)	
Methanol	9.4e-13	9.4e-13				A	0.14	4.0	0.8	0.14	3.0	0.6	1.3
Ethanol	3.3e-12	3.3e-12				A	0.41	8.0	3.4	0.41	4.0	1.7	2
Propylene Glycol	2.2e-11	2.2e-11				A	0.97	12.0	7.4	0.94	4.1	2.5	3
Ethyl Acetate	1.7e-12	1.7e-12				B	0.24	15.8	2.1	0.24	5.3	0.7	3
t-Butyl Acetate	4.4e-13	4.4e-13				B	0.07	15.2	0.4	0.07	5.4	0.2	3
Dibasic Ester DBE-4	1.5e-12	1.5e-12				B	0.21	15.8	1.1	0.22	2.9	0.2	5
Dibasic Ester DBE-5	3.5e-12	3.5e-12				B	0.43	16.7	2.1	0.43	3.1	0.4	5
N-Methyl-2-Pyrrolidone	2.2e-11	2.2e-11		1.3e-13		NP	0.97	20.0	9.4	0.93	5.1	2.3	4
Formaldehyde	2.0e-11	9.7e-12			7.7e-5	P	0.96	11.0	16.8	0.94	4.5	6.7	3
Acetaldehyde	1.6e-11	1.6e-11			6.0e-6	P	0.93	22.0	22.2	0.89	6.5	6.3	4
C3 Aldehydes	2.0e-11	2.0e-11			6.0e-6	P	0.96	33.0	26.2	0.93	9.8	7.5	3
Methyl Glyoxal	3.9e-11	1.7e-11			1.7e-4	P	1.00	33.0	21.9	1.00	20.8	13.8	2
Acetone	3.1e-13	2.3e-13			6.0e-7	P	0.05	33.0	1.3	0.05	11.3	0.5	3
Methyl Ethyl Ketone	1.4e-12	1.2e-12			1.6e-6	P	0.20	35.0	4.6	0.20	10.7	1.4	3
Methyl Isobutyl Ketone	1.4e-11	1.4e-11			1.6e-6	P	0.90	35.0	15.1	0.86	8.4	3.5	4
Biacetyl	3.6e-11	2.3e-13			2.8e-4	P	1.00	35.0	19.5	1.00	31.8	17.7	1.1
Methyl Nitrite	2.8e-10	1.2e-13			2.2e-3	P	1.00	11.0	8.7	1.00	10.2	8.0	1.1
Chloropicrin	8.5e-12	0.0e+0			6.5e-5	P	0.74	11.0	2.4	0.74	4.8	1.0	2

[a] MIR values calculated using an updated version of the SAPRC mechanism (Carter et al, 1997a.).

[b] Codes for methods for deriving upper limit mechanistic reactivities (MRs) are as follows, where nC is the number of carbons and kOH is the OH radical rate constant in units of cm^3 molec^{-1} s^{-1}.

A: Alkane or saturated oxygenate containing only OH or -O- groups: Max MR = MIN [35, 4 x nC, 19.5 - 8.9 x exp(-3.9x1010 x kOH)]

B: Oxygenate containing only -CO-, -OH, or -O- groups: Max MR = MIN [35, 4 x nC, 28.5 - 14.5 x exp(-2.5x1010 x kOH)]

NP: Other non-photoreactive compound: Max MR = MIN [45, 4 x nC]

P: Photoreactive or possibly photoreactive compound: Max Mr = MIN [45, 11 x nC]

KR = kinetic reactivity; MR = mechanistic reactivity (molar basis), MIR = incremental reactivity (gram basis).

[c] KR = kinetic reactivity; MR = mechanistic reactivity (molar basis), MIR = incremental reactivity (gram basis).

[d] Upper limit estimates derived as discussed in the text.

[e] Calculated using the best estimate mechanism for the compound.
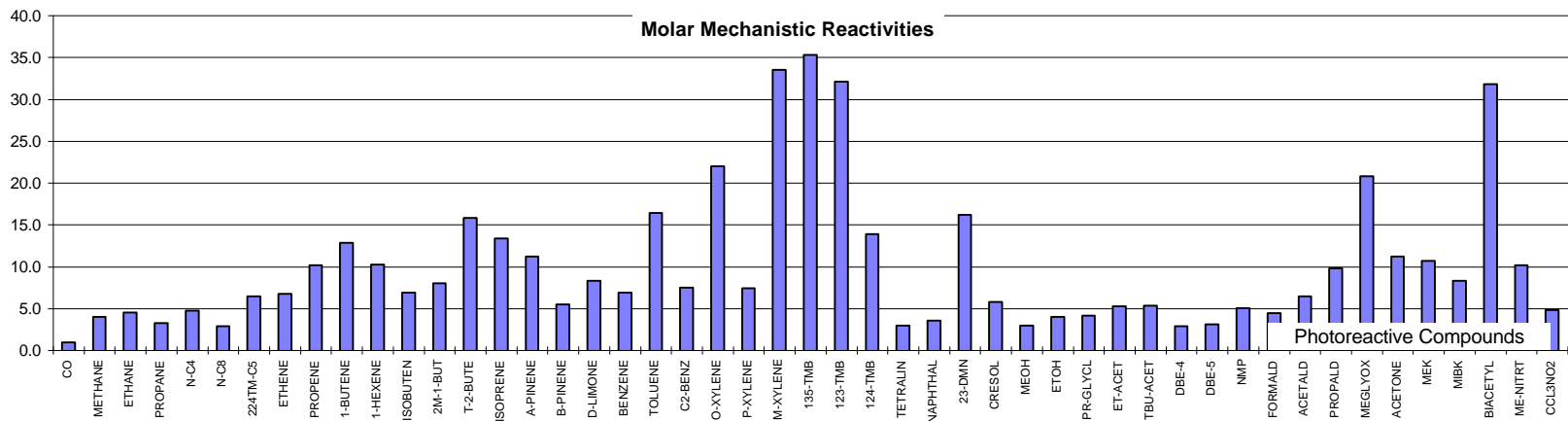
Figure 1.   Plots of calculated mechanistic reactivities, in units of moles ozone formed per mole VOC reacted, for selected compounds in the Averaged Conditions MIR scenario. Compounds are given in the same order as listed in Table 1.
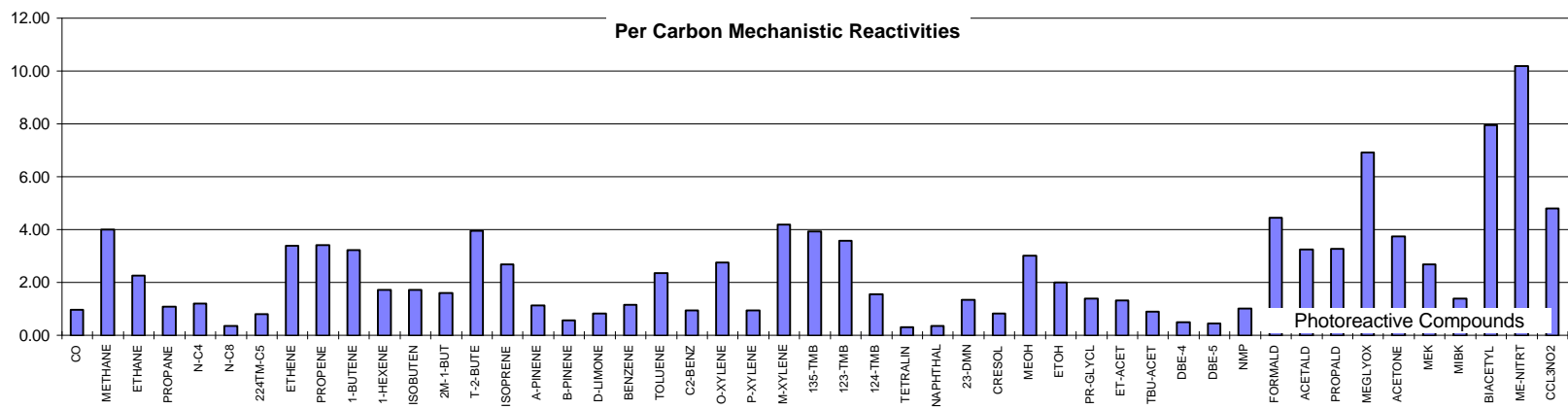
Figure 2.   Plots of calculated mechanistic reactivities, in units of moles ozone formed per mole carbon VOC reacted, for selected compounds in the Averaged Conditions MIR scenario. Compounds are given in the same order as listed in Table 1.

Table 2. Mechanistic reactivities of the major pure mechanism species affecting reactivities of non-photoreactive saturated hydrocarbons or oxygenates, and mechanistic reactivities of the mechanisms used for upper limit reactivity estimates for such compounds.

Pure Mechanism	Yields in Upper Limit Mech's		MIR Mechanisitc Reactivity (Mol O_3 / Mol Pure Mechanism Species)		
	A	B			
OH Rate Consttant (cm^3 molec^{-1} s^{-1})			2.0e-12	2.0e-11	6.8e-11
Methyl Glyoxal Formation		0.5	9.5	13.4	17.2
Higher Aldehyde Formation	1.0	1.0	4.1	6.3	8.1
Acetaldehyde Formation			2.6	4.1	5.2
Formaldehyde Formation	1.0	1.0	2.1	3.0	3.8
Higher Ketone Formation	1.0	1.0	0.8	1.4	1.9
Acetone Formation			0.2	0.4	0.5
Organic Nitrates (radical termination)			-2.3	-2.7	-3.6
HO$_2$ Radicals (radical propigation)	1.0	1.0	1.0	1.2	1.3
Extra NO to NO$_2$ Conversions	3.0	3.0	1.1	1.2	1.3
Mechanism A Upper Limit Mechanistic Reactivities (no carbonyl group)			11.3	15.4	18.9
Mechanism B Upper Limit Mechanistic Reactivities (with carbonyl group)			16.0	22.1	27.4