Estimation of Upper Limit
Relative Ozone Impacts of VOCs

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Abstract

The current practice for the U.S. EPA is to consider exempting volatile organic compounds (VOCs) from regulation as tropospheric ozone precursors if they can be shown to have lower or similar ozone impacts as does ethane. This paper discusses a procedure to estimate upper limit ozone impacts of compounds relative to ethane (or any other compound chosen to define the low-reactivity standard), if only the atmospheric reaction rate constants are known. This is based on deriving upper limits for the two factors which determine the ozone impact of a compound in a pollution episode: its *kinetic reactivity*, or the fraction of emitted VOC which reacts during the episode, and its *mechanistic reactivity*, the amount of ozone formed per molecule of VOC which reacts. Upper limit relative kinetic reactivities are derived from the ratio of the OH radical rate constants, with corrections being made if the VOC reacts with O_3, NO_3 radicals, or by photolysis. Upper limit relative mechanistic reactivities are obtained from calculated relative mechanistic reactivities for a variety of VOCs for various one day ozone episodes. The minimum information needed for making such estimates is discussed, and examples are given for several representative low reactivity compounds.

Implications

The exemption of a compound from regulation as a VOC ozone precursor can have major benefits to its producers and users, but inappropriate exemptions may have adverse environmental impacts. For a compound to be considered for exemption, it must be shown that it reacts too slowly for it to possibly have a significant ozone impact, or else environmental chamber and chemical mechanism evaluation studies, which are generally costly and time-consuming, need to be carried out to assess its likely ozone impacts. This paper discusses how one can determine whether the available reaction rate information is sufficient to determine if a compound is appropriate for exemption, without the need for additional studies.

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Introduction

Volatile organic compounds (VOCs) which can be shown to have sufficiently low ozone impact (i.e., reactivity) can be exempted from regulations as an ozone precursor. How low an ozone impact is appropriate to establish exemption is uncertain, but at present the EPA's informal policy is to use the reactivity of ethane in this regard[1]. Thus, if a VOC can be shown to have a lower or similar ozone impact as ethane, then it can be considered an appropriate candidate for exemption. Ethane is used as the standard primarily for historical reasons, though because of its low reactivity it is probably not inappropriate for this purpose.

Although ozone impacts of VOCs can be quantified in a number of ways, for regulatory applications the relevant measure is the effect of changing its emissions on ozone formation in the atmosphere. This is measured by the *incremental reactivity* of the VOC, which is defined as the change in ozone caused by adding a small amount of the VOC to the emissions, divided by the amount added[2,3]. Incremental reactivities are not inherent properties of the VOC because also they depend on the environment where it is emitted. Thus magnitudes and (to a lesser, but non-negligible, extent) ratios of incremental reactivities will vary from scenario to scenario. In addition, they will be different in environmental chamber experiments than they are in the atmosphere[2-4], which means that atmospheric incremental reactivities cannot be measured directly in the laboratory.

Because of this, the only practical way to determine relative ozone impacts in the atmosphere is to calculate them using computer airshed models. However, because of the uncertainties in atmospheric reaction mechanisms of most VOCs, such model predictions must be considered to be too uncertain to use for regulatory applications unless it has been shown that the chemical mechanism used in the model is capable of accurately predicting the ozone impacts of the VOCs in question. The only way to assure this is to conduct environmental chamber experiments employing the VOCs range of chemical conditions representing those in the atmosphere, and determine if model predictions are consistent with the results.

Because relative ozone impacts can vary with conditions, the incremental reactivities must be calculated for a range of atmospheric conditions which are relevant for assessing VOC regulations for ozone control; use of a single reactivity scale is not sufficient for this purpose. If the model calculations predict that a candidate VOC always or usually has lower or equal ozone impact than equal masses of ethane, and if the accuracy of the mechanism for the VOC has been experimentally verified (or at least

has been shown not to significantly underpredict its the ozone impact), then it can be concluded that the VOC is likely to be less reactive than ethane, and thus is an appropriate candidate for exemption under the present criteria. Of course, there will always be borderline cases, and the EPA will need to establish appropriate criteria to use for VOCs which have higher ozone impacts than ethane under some conditions, and lower under others.

For most VOCs, obtaining reliable estimates of ozone impacts by modeling is relatively expensive and time consuming. This is because experimentally verified mechanisms have only been developed for a limited number of compounds, and if such a mechanism is not available, the necessary environmental chamber experiments and mechanism development work would have to be carried out first. However, many VOCs react so slowly in the atmosphere that there is no reasonable chance that they could have a greater ozone impact than ethane regardless of the nature of their atmospheric reactions. This is because model calculations have shown that there is a maximum amount of ozone formation that the reactions of a given amount of VOC can cause[2,3]. Thus, if a compound can be shown to react sufficiently slowly, it can be appropriately exempted on the basis of low reactivity without the need to carry out a comprehensive mechanism development and reactivity modeling study.

Given below are suggested procedures which can be employed to estimate upper limit ozone impacts for VOCs for which the only available information concern their atmospheric reaction rate constants.

Information Required

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. 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 abstractible 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[5,6].

Methods exist for estimating OH radical rate constants for many compounds which are usually accurate to within a factor of 2 or better[7]. However, exceptions exist, and estimates should not be relied upon for establishing exemption without the benefit of direct measurements (or at least upper limit determinations) to confirm the estimates.

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[8], and is updated by Atkinson[6].

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[6,9].

Photolysis. 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 ≥ 290 nm, and the actinic fluxes for direct overhead sunlight for clear-sky conditions, assuming unit quantum yields. The actinic fluxes given by Peterson[10] 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 $\lambda \geq$ 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[11] and IUPAC[12] 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[13].

Factors Affecting Reactivity

For upper limit estimation purposes, it is useful to think of the incremental reactivity of a VOC as a product of three factors, as follows[2]:

$$
\begin{matrix}
\text{Incremental} & & \text{Kinetic} & & \text{Mechanistic} & & \text{Mass Conv-} \\
\text{Reactivity} & = & \text{Reactivity} & \cdot & \text{Reactivity} & \cdot & \text{ersion Factor} \\
\text{(Ozone per} & & \text{(VOC reacted} & & \text{(moles } O_3 & & \text{(moles VOC} \\
\text{mass VOC} & & \text{/VOC emitted)} & & \text{/mole VOC} & & \text{/mass VOC)} \\
\text{emitted)} & & & & \text{reacted)} & &
\end{matrix}
\qquad (1)
$$

The <u>kinetic reactivity</u> 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 as discussed below 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.

The <u>mechanistic reactivity</u> 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 this 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.

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 <u>mass conversion factor</u> is applied to place the incremental reactivities on a mass VOC basis. It is inversely proportional to the VOC's molecular weight.

Note that the quantity of interest in considering VOC exemptions is not the absolute incremental reactivity, but the incremental reactivity relative to ethane (or relative to whatever other low-reactivity compound which is being used as the standard). From Equation (1) we have,

$$
\begin{matrix} \text{Ozone Impact} \\ \text{Relative to} \\ \text{Ethane (mass} \\ \text{basis)} \end{matrix}
=
\begin{matrix} \text{Kinetic} \\ \text{Reactivity} \\ \text{relative} \\ \text{to ethane} \end{matrix}
\cdot
\begin{matrix} \text{Mechanistic} \\ \text{Reactivity} \\ \text{relative} \\ \text{to ethane} \end{matrix}
\cdot
\frac{MWt^{Ethane}}{MWt^{VOC}}
\qquad (2)
$$

The last term is simply a ratio of molecular weights. Estimation of upper limits for the other factors are discussed below.

Estimation of Maximum Kinetic Reactivity Ratios

If the VOC, like ethane, reacts significantly only with OH radicals, then for a given scenario the fraction reacted can be estimated by

$$
\begin{aligned}
\text{Kinetic Reactivity} \approx\ & (1 - e^{-kOH \cdot IntOH}) \\
\approx\ & kOH \cdot IntOH \quad \text{(if } kOH \cdot IntOH \ll 1) \qquad (3)
\end{aligned}
$$

where kOH is the VOC's OH radical rate constant, and IntOH is a scenario-dependent parameter which is related to, but is not exactly the same as, the integrated OH radical levels[2]. Fortunately, for slowly reacting VOCs such as ethane and any VOC which would be a reasonable candidate for exemption on the basis of slow reaction rates, the kinetic reactivity is approximately proportional to the OH radical rate constant. Thus, for relatively slowly reacting VOCs which react primarily with OH radicals, the kinetic reactivity relative to ethane is simply the ratio of their OH radical rate constants.

$$
\begin{matrix} \text{Kinetic Reactivity of} \\ \text{VOC relative to Ethane} \end{matrix}
\approx kOH^{VOC} / kOH^{Ethane}
\qquad (4)
$$

This simple relation does not work if the VOC photolyses or reacts with O_3 or NO_3 radicals. However, for slowly reacting VOCs such as ethane and reasonable exemption candidates, the kinetic reactivity should still be approximately proportional to the atmospheric reaction rates. Since reaction rates vary throughout the day, a somewhat better indication of the kinetic reactivity would be the integrated reaction rates, which would be approximately proportional to the rate constant times the integrated concentration of the reactant with which the VOC reacts. Thus,

$$\text{Kinetic Reactivity of VOC Relative to Ethane} \approx \frac{kOH^{VOC} \cdot IntOH + kO_3^{VOC} \cdot IntO_3 + kNO_3^{VOC} \cdot IntNO_3 + \int kPhot^{VOC}dt}{kOH^{Ethane} \cdot IntOH} \quad (5)$$

The integrated levels of OH radicals, O_3, and NO_3 radicals will depend on scenario conditions, and the number of days in the episode being considered. With regard to the latter, it is sufficient to consider only single-day episodes, since it is only ratios of these values which are significant in this context, which would be independent of the number of days in the episode if all days are the same. Table I summarizes these quantities calculated for the set of one-day EKMA model scenarios[14] developed by the EPA to represent various ozone non-attainment in the United States for planning purposes[15]. These scenarios were also used to derive various incremental reactivity scales[3], and should be sufficient to provide an indication of how these quantities may vary under conditions where ozone formation is of concern.

Table I also shows the suggested value for use in upper limit estimates of reactivity relative to ethane. Note that to be consistent with the units for IntOH, IntO$_3$, and IntNO$_3$ shown on the table, the units for the rate constants should be cm^3 molec^{-1} s^{-1}. The integrated OH levels did not vary significantly among the scenarios, and use of the average value is recommended. However, for integrated NO_3 and ozone, which are more variable from scenario to scenario, it is recommended that values closer to the upper limits be used, to obtain upper limits for the kinetic reactivity ratio relative to ethane. However, the high ozone Los Angeles scenario was not used in deriving the upper limit recommendations, because ozone levels in excess of 0.5 ppm are no longer characteristic of the situation in Los Angeles or any other ozone exceedence area in the United States.

If the compound photolyses, it is also necessary to estimate $\int kPhot^{VOC}dt$, the integrated photolysis rate. The recommendation for an upper limit is to use 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[10]) 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, unit quantum yields at all wavelengths should be assumed. The integrated photolysis rate can then be approximated from the calculated $kPhot^{VOC}_{max}$ using:

$$\int kPhot^{VOC}dt \approx (\text{length of time in scenario}) \cdot 0.8 \cdot kPhot^{VOC}_{max} \approx 3.0\text{x}10^4 \text{ sec} \cdot kPhot^{VOC}_{max} \tag{6}$$

where the length of time should be the same as that used when computing IntOH, $intO_3$, and $IntNO_3$, which is 10 hours for the EKMA scenarios shown on Table I. To be consistent with the units shown above, the units of $kPhot^{VOC}_{max}$ should be s^{-1}. The 0.8 factor is the ratio of the average to the maximum photolysis rate, and was derived by comparing integrated with maximum NO_2 photolysis rates calculated for Atlanta, GA in the summertime. 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 0.8 factor is considered appropriate for upper limit estimates.

Therefore, for VOCs which react via other means besides just with OH radicals, equations (4-6) can be combined and re-arranged to yield a modified version of Equation (4),

$$\begin{matrix}\text{Kinetic Reactivity of} \\ \text{VOC relative to Ethane}\end{matrix} \approx \text{Effective } kOH^{VOC} / kOH^{Ethane} \tag{7}$$

where

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

if the recommended values for IntOH, $IntO_3$, and $IntNO_3$ shown on Table I are used, then the effective OH radical rate constant is given by

$$\text{Effective } kOH^{VOC} \approx kOHVOC + 5\text{x}10^5 \, kO_3^{VOC} + 5 \, kNO_3^{VOC} + 1.5\text{x}10^{-7} \, kPhot^{VOC}_{max}. \tag{8}$$

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where the units of the bimolecular rate constants are cm^3 $molec^{-1}$ s^{-1}, and the units of $kPhot_{max}^{VOC}$ 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.

Estimation of Maximum Mechanistic Reactivity Ratios

Upper limit estimates for mechanistic reactivities can be obtained from examining the distribution of mechanistic reactivities for a sufficiently wide variety of VOCs under a wide variety of conditions. The updated[15] version of the SAPRC-90[16] 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)[17] 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.

With regard to scenario conditions, the main factors affecting mechanistic reactivities are the efficiency of ozone formation resulting from the NO to NO_2 conversions in a VOCs oxidation reactions, and the extent to which the chemical conditions in the scenario are sensitive to effects of VOCs on radical and NO_x levels[2,3]. The 39 one day EKMA scenarios developed by the EPA to represent various ozone non-attainment areas[15], together with the various adjusted NO_x versions of these scenarios developed to calculate various reactivity scales[3], should provide a sufficiently varied set of chemical conditions for likely ranges of mechanistic reactivities for various VOCs.

Figure 1 shows the mechanistic reactivities relative to ethane for the 30 VOCs which were calculated to have the highest mechanistic reactivities. Values are shown for relatively high NO_x Maximum Incremental Reactivity (MIR)[3], the moderate NO_x Maximum Ozone Incremental Reactivity (MOIR)[3], and for the base case EPA scenario[3,15] which the VOC had the highest mechanistic reactivity relative to ethane (Max Base). The highest mechanistic reactivity ratio appears to be ~6.5, which is observed for the trialkyl benzenes. Methylglyoxal, furan, chloropicrin, methyl nitrite, dialkyl benzenes and internal olefins also have high per-molecule mechanistic reactivities being in the range of 4-6. Based on these results, it is unlikely that any compound will have a mechanistic reactivity greater than ~7. This then could serve as a conservative value for upper limit mechanistic reactivity estimation purposes.

However, Figure 1 also shows that the mechanistic reactivities for these high-mechanistic-reactivity compounds tend to increase as the size of the molecule increases, particularly if highly photoreactive compounds such as methyl nitrite and methylglyoxal are excluded. The trialkyl benzenes are the highest molecular weight compounds with high mechanistic reactivities whose reactivities have been calculated, and the possibility that larger compounds with similar mechanisms may have higher mechanistic reactivities cannot be excluded. This suggests that mechanistic reactivity divided by the number of carbons may provide a more precise and realistic indication of the likely upper limit values, which may give more realistic upper limit estimates for lower molecular weight compounds, and be less likely to underestimate mechanistic reactivities for molecules which are larger than those whose reactivities have been calculated. Figure 2 shows plots of the calculated mechanistic reactivities relative to ethane, divided by the number of carbons, for the 30 compounds where this was calculated to have the highest value.

From Figure 2 it can be seen that the highly photoreactive compounds methyl nitrite and methyl glyoxal have mechanistic reactivity / carbon number values than all the other compounds, and perhaps should be considered separately. If these are excluded, then methane and furan have the highest values at ~1.25, and a large number of other compounds, including those calculated to have the highest mechanistic reactivities, have values in the 0.5 - 1 range. This suggests that, for non-photoreactive compounds (i.e., compounds where $kPhot_{max}^{VOC} \ll$ Effective kOH^{VOC}), the upper limit mechanistic reactivity relative to ethane, MRR^{max}, can be estimated as

$$MRR^{max} \approx 1.25 \ N_C \tag{9}$$

where N_C is the number of compounds in the molecule. If the compound is photoreactive, i.e., if $kPhot_{max}^{VOC}$ is a non-negligible fraction of Effective kOH^{VOC}, then molecular mechanistic reactivity could be as high as 5, based on the data for chloropicrin and methyl nitrite. For such compounds, the recommendation is to use

$$MRR^{max} \approx MAX \ (5, \ 1.25 \ N_C) \tag{10}$$

to estimate the upper limit mechanistic reactivity relative to ethane.

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Summary of Recommendations

Before a VOC can be considered for exemption on the basis of low reactivity, rate constants, or upper limits thereof, should be obtained for the VOC's reaction with OH radicals, ozone, and NO_3. In the absence of such data, convincing argument should be given that these reactions should be negligible. In addition, the compound must be shown not to have significant absorption in the UV at wavelengths above 190 nm, or the absorption cross sections need to be measured and upper limit photolysis rates calculated as discussed above. If no information is available concerning upper limit quantum yields, then unit quantum yields should be used in this calculation. Obviously, the molecular weight of the compound must also be known.

From Equations (2) and (7), we obtain:

$$\text{Upper Limit Reactivity Relative to Ethane (mass basis)} \approx \frac{\text{Effective } kOH^{VOC}}{kOH^{Ethane}} \cdot MRR^{max} \cdot \frac{MWt^{Ethane}}{MWt^{VOC}} \tag{11}$$

where MRR^{max} is calculated from Equation (9) if the compound does not photolyze, and (10) if it does, and "Effective kOH^{VOC}" is simply the OH radical rate constant if the compound reacts only with OH radicals, or is calculated using Equation (7) if not. Given $kOH^{Ethane} = 2.5 \times 10^{-13}$ cm^3 molec^{-1} s^{-1} [12] and $MWt^{ethane} = 30.07$ gm/mole, and assuming that effective kOH^{VOC} and MWt^{VOC} are in the same units, then equation (10) yields:

$$\text{Upper Limit Reactivity Relative to Ethane (mass basis)} \approx MRR^{max} \cdot \frac{\text{Effective } kOH^{VOC} / MWT^{VOC}}{8.3 \times 10^{-15}} \tag{12}$$

where the units of Effective kOH^{VOC} must be cm^3 molec^{-1} s^{-1}. If the compound reacts only with OH radicals, then this can be simplified and combined with Equation (9) to yield,

$$\text{Upper Limit Reactivity Relative to Ethane (mass basis)} \approx \frac{kOH^{VOC} \cdot (N_C / MWT^{VOC})}{6.6 \times 10^{-15}} \tag{13}$$

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where the units of kOH^{VOC} must be cm^3 molec^{-1} s^{-1}.

Thus we conclude that if (effective kOH^{VOC} / MWt^{VOC}) < MR^{max} x 8.3 x 10^{-15} cm^3 AMU^{-1} s^{-1}, or if the compound reacts only with OH and (kOH^{VOC} x N_C / MWT^{VOC}) is less than 6.6 x 10^{-15} cm^3 AMU^{-1} s^{-1}, then it is highly unlikely that the VOC will have a greater impact on ozone formation than does ethane. If the appropriate quantity is higher than this, then model calculations, based on an experimentally verified mechanism for the VOC, are necessary before any conclusions can be made concerning the VOC's reactivity relative to ethane.

Examples of Application

Given below are four examples of application of this method to estimation of upper limit reactivities: methyl bromide, 1-bromo propane, methyl iodide, and bromoform.

Methyl Bromide. Methyl bromide has an OH radical rate constant of 2.9 x 10^{-14} cm^3 molec^{-1} s^{-1} at 298 K[12], one carbon, and a molecular weight of 94.93 gm/mole. Based on data for other halogenated compounds it is unlikely to react significantly with O_3 or NO_3 radicals or to photolyze. Therefore Equation (13) can be used to estimate its upper limit reactivity. Its (kOH x N_C / MWt) ratio is 3.05 x 10^{-16}, and thus from Equation (13), its upper limit reactivity relative to ethane is calculated to be 0.05. This means that the upper limit mass-based reactivity for this compound is approximately 20 times less than that of ethane. Therefore, it is probably safe to conclude, without the benefit of additional information, that this compound is less reactive than ethane.

1-Bromo Propane. This compound has an OH radical rate constant of 1.18 x 10^{-12} cm^3 molec^{-1} s^{-1} [18], has 3 carbons, and a molecular weight of 123.0 gm/mole. Like methyl bromide, it is unlikely to photolyze or react significantly with O_3 or NO_3 radicals. Therefore, Equation (13) again is applicable. Its (kOH x N_C / MWt) ratio is 2.9 x 10^{-15}, which means that it has an upper limit reactivity which is over 4 times greater than that for ethane. Therefore, it would not be prudent to conclude that this compound has a comparable or lower reactivity than ethane without the benefit of model calculations using an experimentally verified mechanism for this compound.

Methyl Iodide. This compound has an OH radical rate constant of 7.2 x 10^{-14} cm^3 molec^{-1} s^{-1} [12], and probably does not react to a significant extent with O_3 or NO_3. However, its absorption cross sections,

given in the IUPAC evaluation[12], give a maximum atmospheric photolysis rate of 7.6 x 10^{-6} s^{-1}. From Equation (7), this gives an Effective kOH of 1.2 x 10^{-12} cm^3 $molec^{-1}$ s^{-1}, with essentially all of the kinetic reactivity due to photolysis. It has a molecular weight of 141.9 and has one carbon. Since this is a photoreactive compound, Equation (10) is used to estimate its upper limit mechanistic reactivity to be 5, and Equation (12) is applicable for estimating its upper limit reactivity. From Equation (12), and using MRR ≤ 5, the upper limit reactivity for this compound is estimated to be ~5 times that of ethane. Therefore, it would not be prudent to conclude that this compound is necessarily less reactive than ethane without the benefit of data concerning the its actual impact on O_3 formation.

Bromoform. The rate constant for the reactions of OH radicals with bromoform ($CHBr_3$) is not known, but, based on data for CH_3Cl, CH_3Br, CH_2Cl_2 and CH_2Br_2[12], it is expected to be no greater to that for chloroform ($CHCl_3$), which is 1 x 10^{-13} cm^3 $molec^{-1}$ s^{-1}. We assume for the sake of discussion that this is the case, though this would need to be confirmed experimentally before regulatory decisions concerning this compound are made. Bromoform is not expected to react significantly with O_3 or NO_3, but its absorption cross-sections given in the IUPAC evaluation[12] give a maximum atmospheric photolysis rate of 1.6 x 10^{-6} s^{-1}. From Equation (7), this gives an effective kOH of 3.4 x 10^{-13} cm^3 $molec^{-1}$ s^{-1}. It has a molecular weight of 252.7 and has one carbon. Since, like methyl iodide, this is a photoreactive compound, Equations (10) and (12) are applicable for estimating its upper limit reactivity. This yields an upper limit reactivity for bromoform of ~0.85 times that of ethane. Therefore, it might be reasonable to conclude that this compound is unlikely to be more reactive than ethane.

Discussion

The recommendations for estimating upper limit reactivities relative to ethane developed primarily to assist the EPA in considering VOC exemption petitions on the basis of "negligible" ozone impact, given the apparent policy of using ethane as the standard in this regard. However, if a different compound (or set of compounds) is used as the standard, then similar considerations to those discussed above could be used for the purposes of estimating upper limit reactivities. A discussion of whether ethane is an appropriate compound to use as the standard in this regard, or the extent to which other factors such as toxicity should be considered in VOC exemption petitions, is beyond the scope of this paper.

Note that regardless of what compound is used as the standard, a more precise estimate of upper limit reactivities relative to that standard can be obtained by estimating upper limit *ratios* of reactivities

of the compounds relative to the standard VOC, rather than estimating upper limit *absolute* reactivities, and comparing them with absolute reactivities of the standard compound. This is because ratios of reactivities would be expected to be much less variable with environmental conditions than absolute reactivities. If estimates had to be given in terms of absolute reactivities, the margin of error which would have to be used to account for this variability would reduce the number of compounds which could be judged to be less reactive than the standard compound based on kinetic data alone.

The recommendations given in this work are based on reactivity calculations for a wide variety of compounds in a variety of one-day scenarios. While it is considered unlikely that upper limit reactivities relative to ethane would be significantly higher if multi-day scenarios were considered, this possibility has not been fully evaluated. In addition, it should be pointed out that the upper limit mechanistic reactivities are driven primarily by calculated reactivities for aromatic hydrocarbons, methyl glyoxal, chloropicrin, methyl nitrite, and methane. The other classes of compounds which were considered were primarily alkanes, olefins, and various relatively low molecular weight oxygenates[3,16]. If a compound is expected to possibly have a significantly different mechanism than any compound in this group, then a wider margin of uncertainty should be given to these upper limit reactivity estimates before concluding that the compound will be less reactive than ethane (or whatever the standard compound is) without the benefit of additional data. For example, at present there are no evaluated mechanisms for bromine-containing compounds, and the reactions of a bromoform molecule might reasonably be expected to introduce at least two, and possibly more, Br. atoms into the system. Even though, based on reactivities calculated for compounds presently in the SAPRC mechanism[15,16], it is calculated that bromoform has an upper limit reactivity which is 0.6 that of ethane, it is probably prudent to add a margin of uncertainty and not exclude the possibility that it may in fact be somewhat more reactive without at least some data concerning the ozone impacts of such compounds.

References

1.   B. Dimitriades "Scientific Basis for the VOC Reactivity Issues Raised by Section 183(e) of the Clean Air Act Amendments of 1990," J. Air Waste Manage. Assoc. <u>46</u>, 963-970 (1996).

2.   W. P. L. Carter and R. Atkinson "A Computer Modeling Study of Incremental Hydrocarbon Reactivity", Environ. Sci. and Technol., <u>23</u>, 864 (1989).

3.   W. P. L. Carter "Development of Ozone Reactivity Scales for Volatile Organic Compounds," J. Air & Waste Manage. Assoc., 44, 881-899 (1994).

4.   W. P. L. Carter, D. Luo, I. L. Malkina, and J. A. Pierce "Environmental Chamber Studies of Atmospheric Reactivities of Volatile Organic Compounds. Effects of Varying ROG Surrogate and NO$_x$," Final report to Coordinating Research Council, Inc., Project ME-9, California Air Resources Board, Contract A032-0692, and South Coast Air Quality Management District, Contract C91323. March 24, 1995. (This report can be downloaded from the Internet. See http://cert.ucr.edu/~carter/ bycarter.htm.)

5.   R. Atkinson "Kinetics and Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical with Organic Compounds," J. Phys. Chem. Ref. Data, Monograph no 1 (1989).

6.   R. Atkinson "Gas-Phase Tropospheric Chemistry of Organic Compounds," J. Phys. Chem. Ref. Data, Monograph No. 2 (1994).

7.   E. S. C. Kwok, and R. Atkinson "Estimation of Hydroxyl Radical Reaction Rate Constants for Gas-Phase Organic Compounds Using a Structure-Reactivity Relationship: An Update," Atmos. Environ 29, 1685-1695 (1995).

8.   R. Atkinson and W. P. L. Carter "Kinetics and Mechanisms of the Gas-Phase Reactions of Ozone with Organic Compounds under Atmospheric Conditions," Chem. Rev. 1984, 437-470 (1984).

9.   R. Atkinson "Kinetics and Mechanisms of the Gas-Phase Reactions of the NO$_3$ Radical with Organic Compounds," J. Phys. Chem. Ref. Data, 20, 459-507 (1991).

10.   J. T. Peterson "Calculated Actinic Fluxes (290 - 700 nm) for Air Pollution Photochemistry Applications", EPA-600/4-76-025, June, 1976.

11.   NASA "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation Number 11," JPL Publication 94-26, Jet Propulsion Laboratory, Pasadena, California, December, 1994.

12. R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, M. J. Rossi, and J. Troe "Evaluated Kinetic, Photochemical and Heterogeneous Data for Atmospheric Chemistry: Supplement V., IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry," J. Phys. Chem. Ref. Data, 26, 521-1011 (1997).

13. J. G. Calvert and J. N. Pitts, Jr. Photochemistry, John Wiley and Sons, New York (1966).

14. EPA "Guideline for Using the Carbon Bond Mechanism in City-Specific EKMA," EPA-450/4-84-005, February, 1984.

15. K. Baugues "Preliminary Planning Information for Updating the Ozone Regulatory Impact Analysis Version of EKMA," Draft Document, Source Receptor Analysis Branch, Technical Support Division, U. S. Environmental Protection Agency, Research Triangle Park, NC, January, 1990.

15. W. P. L. Carter "Computer Modeling of Environmental Chamber Measurements of Maximum Incremental Reactivities of Volatile Organic Compounds," Atmos. Environ., 29, 2513-2517 (1995).

16. W. P. L. Carter "A Detailed Mechanism for the Gas-Phase Atmospheric Reactions of Organic Compounds," Atmos. Environ., 24A, 481-518 (1990).

17. W. P. L. Carter, D. Luo, and I. L. Malkina "Investigation of the Atmospheric Reactions of Chloropicrin," Atmos. Environ., 31, 1425-1439 (1997).

18. T. Donaghy, I. Shanahan, M. Hande and S. Fitzpatrick, Int. J. Chem. Kinet. 25, 273 (1993).

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Table I. Maximum and integrated concentrations of OH radicals, ozone, and NO$_3$ radicals in various 1-day ozone exceedence scenarios used for VOC reactivity assessment, and recommended integrated concentrations for use in maximum relative reactivity estimates.

| Scenario		Maximum Reactants (ppm)			Integrated Reactants (molec cm^{-3} sec)		
		OH	O$_3$	NO$_3$	IntOH	IntO$_3$	IntNO$_3$
Recommended for Maximum Relative Reactivity Estimates:					2.0e+11	1.0e+17	1.0e+12
Averaged Conditions							
MIR		3.4e-7	0.18	3.2e-6	1.8e+11	8.5e+16	7.4e+11
MOR		6.6e-7	0.23	3.1e-6	3.1e+11	1.2e+17	9.6e+11
EBIR		5.6e-7	0.22	2.1e-6	3.1e+11	1.3e+17	7.9e+11
Base Case							
Average		5.7e-7	0.23	3.9e-6	3.0e+11	1.2e+17	1.1e+12
Std.Dev		20%	35%	155%	18%	32%	121%
Maximum		7.8e-7	0.57	3.7e-5	3.8e+11	3.0e+17	8.8e+12
Minimum		1.7e-7	0.13	5.9e-7	1.1e+11	7.1e+16	2.6e+11
LOS	CA	5.0e-7	0.57	3.7e-5	2.2e+11	3.0e+17	8.8e+12
NEW	NY	5.0e-7	0.36	4.3e-6	2.6e+11	2.2e+17	1.9e+12
BAL	MD	6.5e-7	0.32	4.6e-6	2.9e+11	1.5e+17	1.8e+12
SAI	MO	6.1e-7	0.32	5.5e-6	2.8e+11	1.5e+17	1.7e+12
SFO	CA	1.7e-7	0.31	1.1e-5	1.1e+11	1.1e+17	1.9e+12
HOU	TX	6.9e-7	0.31	6.9e-6	3.5e+11	1.6e+17	1.9e+12
LAK	LA	6.0e-7	0.29	4.8e-6	3.8e+11	1.5e+17	1.3e+12
CHI	IL	4.1e-7	0.28	4.8e-6	2.7e+11	1.7e+17	1.5e+12
WAS	DC	7.0e-7	0.28	4.3e-6	3.5e+11	1.5e+17	1.5e+12
PHO	AZ	5.2e-7	0.27	4.4e-6	2.5e+11	1.4e+17	1.7e+12
CLE	OH	5.6e-7	0.25	2.0e-6	2.9e+11	1.3e+17	9.4e+11
BAT	LA	5.4e-7	0.25	4.6e-6	3.0e+11	1.3e+17	1.0e+12
PHI	PA	7.1e-7	0.24	3.1e-6	3.4e+11	1.2e+17	9.5e+11
BIR	AL	5.3e-7	0.24	3.4e-6	3.1e+11	1.5e+17	1.2e+12
DET	MI	7.1e-7	0.24	2.2e-6	3.5e+11	1.3e+17	9.9e+11
RIC	VA	7.1e-7	0.23	1.6e-6	3.2e+11	1.2e+17	8.1e+11
TAM	FL	6.7e-7	0.23	3.1e-6	3.2e+11	1.1e+17	8.2e+11
MEM	TN	6.5e-7	0.22	2.3e-6	3.7e+11	1.3e+17	8.6e+11
TUL	OK	7.8e-7	0.22	1.7e-6	3.8e+11	1.1e+17	7.5e+11
DAL	TX	5.5e-7	0.21	4.2e-6	2.7e+11	1.0e+17	9.7e+11
IND	IN	6.3e-7	0.21	1.4e-6	3.2e+11	1.1e+17	6.4e+11
LOU	KY	6.8e-7	0.21	1.5e-6	3.8e+11	1.1e+17	6.8e+11
DEN	CO	4.7e-7	0.21	1.6e-6	2.3e+11	1.1e+17	6.2e+11
SAC	CA	6.0e-7	0.20	2.4e-6	3.1e+11	1.0e+17	7.2e+11
CIN	OH	6.8e-7	0.20	1.4e-6	3.1e+11	1.1e+17	6.9e+11
SDO	CA	5.1e-7	0.19	1.1e-5	2.2e+11	1.1e+17	1.2e+12
BOS	MA	6.7e-7	0.19	1.7e-6	3.7e+11	1.2e+17	7.0e+11
ELP	TX	4.6e-7	0.19	2.6e-6	2.2e+11	1.0e+17	6.6e+11
SAL	UT	4.8e-7	0.18	1.2e-6	2.7e+11	1.1e+17	6.1e+11
ATL	GA	5.3e-7	0.18	1.3e-6	3.1e+11	9.7e+16	4.5e+11
AUS	TX	4.7e-7	0.17	1.5e-6	2.7e+11	1.1e+17	5.4e+11
HAR	CT	5.3e-7	0.17	8.5e-7	3.2e+11	1.1e+17	4.7e+11
NAS	TN	5.2e-7	0.17	1.4e-6	3.4e+11	1.0e+17	5.1e+11
POR	OR	5.8e-7	0.16	9.4e-7	3.4e+11	9.2e+16	4.0e+11
JAC	FL	5.4e-7	0.16	9.8e-7	3.1e+11	8.4e+16	3.3e+11
KAN	MO	6.5e-7	0.15	7.9e-7	3.3e+11	9.1e+16	3.9e+11
CHA	NC	4.7e-7	0.14	6.1e-7	3.0e+11	9.7e+16	3.3e+11
MIA	FL	4.4e-7	0.13	5.9e-7	2.6e+11	8.4e+16	2.6e+11
SAN	TX	5.9e-7	0.13	1.6e-6	2.6e+11	7.1e+16	3.9e+11
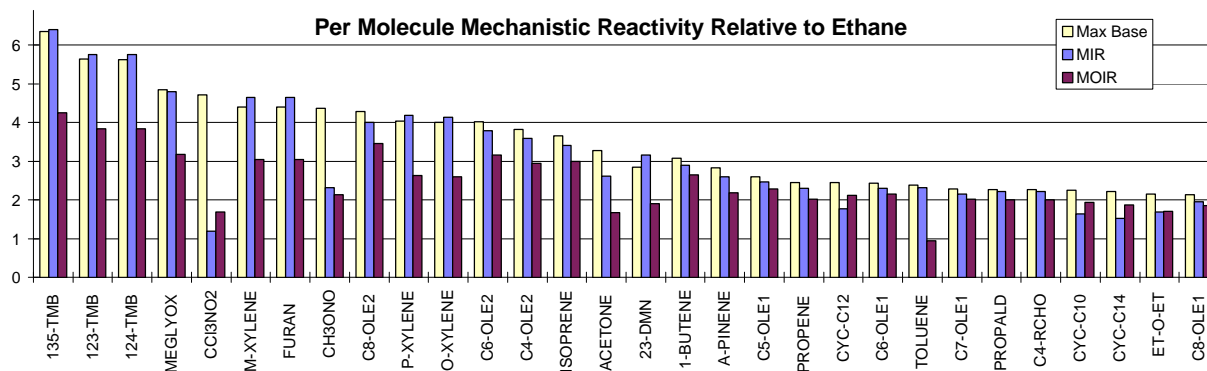
Figure 1. Mechanistic reactivities, relative to ethane, for the 30 types of VOCs with the highest mechanistic reactivities. (Examples of nomenclature: 135-TMB = 1,3,5-trimethyl-benzene; C8-OLE2 = C8 internal alkenes, 23-DMN = 2,3-dimethylnaphthalene, CYC-C12 = C12 cycloalkanes, ET-O-ET = diethyl ether, etc.)
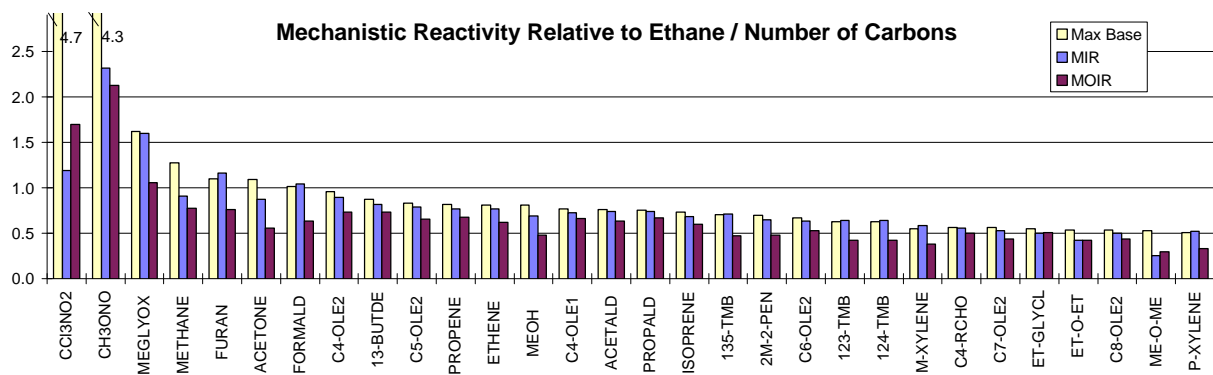

Figure 2. Mechanistic reactivities relative to ethane, divided by the carbon number, for the 30 types of VOCs with the highest values.