

The Ozone Formation Potential of 1-Bromo-Propane

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ABSTRACT

1-BP is a replacement for high-end CFC and HCFC solvents. Its reaction rate constant with the hydroxyl radical OH is, on a weight basis, significantly less than that of ethane. However, the overall smog formation chemistry of 1-BP appears to be very unusual compared to typical volatile organic compounds (VOC) and relatively complex due to the presence of bromine. In smog chamber experiments, compared to what would be expected from ethane, 1-BP initially shows a faster ozone build-up, but then the secondary products that contain bromine tend to destroy ozone such that 1-BP can have a net overall negative reactivity. Alternative sets of reactions are offered to explain this unusual behavior. Follow-on studies are suggested to resolve the chemistry. Using one set of bromine-related reactions in a photochemical grid model shows that 1-BP would be less reactive towards peak ozone formation than ethane now with a trend towards even lower ozone impacts in the future.

INTRODUCTION

The solvent properties and low toxicity of 1-bromopropane alone make it a candidate to replace some high-end CFC and HCFC solvents. However, the “best” replacement solvents must also fit into the ideal "slot" in atmospheric reactivity such that their ozone depletion potentials (ODP) are rendered acceptably low because their global reactivity is high enough to be destroyed in the troposphere before significant quantities of their ozone depleting halogens can enter the stratosphere and yet, at the same time, their atmospheric reactivity must still be

negligibly low towards urban smog formation. 1-BP appears to fall into this ideal reactivity “slot,” but ozone formation reactivity is “a concept that is not easily understood except by those with specialized expertise in the photochemical smog area of science¹.”

Several recent studies have implicated bromine-containing compounds with observed local ozone reductions^{2,3,4} However, these observations have often involved interactions with either chlorine or heterogeneous surfaces. Also the atmospheric conditions of these observations (e.g., in Arctic areas or the Dead Sea) were not typical of the conditions associated with urban smog formation. Nevertheless, some smog-chamber tests⁵ (discussed below) using very large additions of 1-bromopropane to urban mixtures of VOC and nitrogen oxides (NO_x) under smog-like conditions also show evidence of significant ozone reduction reactivity without chlorine or apparent heterogeneous involvement. Yet these same experiments also show some periods of positive ozone “reactivity” due to 1-BP. Hence, for some compounds such as 1-BP even the sign of its “reactivity” can be a difficult concept to clearly define.

U.S. Environmental Protection Agency has attempted to define “reactivity” in a regulatory context since 1977. The EPA definition of reactivity is based on an “ethane k_{OH} bright line” criteria, where an individual VOC can be declared non-reactive if it can be shown to have an ozone-forming potential equal to or less than that of ethane⁶. All other VOC are considered as reactive and are, for regulatory control purposes, treated equally. In practice the ozone-forming comparison to ethane has typically been based on the reaction rate constant (k_{OH}) for the hydroxyl radical (OH) reaction with the candidate VOC compared to the k_{OH} for ethane. Ethane is the standard for a “negligible” threshold of reactivity presumably because its reaction with OH is known to be very slow. For example, if one uses a concentration of OH of 10^6 per cubic centimeter⁷, then the lifetime of ethane would be nearly 50 days. Since 1-BP appears to react only with OH under normal tropospheric conditions, and since 1-BP also reacts as slowly as ethane on a weight basis, then this slow rate alone guarantees that 1-BP will have a low impact on smog formation and is, therefore, a likely candidate for a “negligibly reactive” exemption. To progress beyond “candidate” status, however, it is important to show that once it does react, 1-BP is less reactive towards peak ozone formation than is ethane.

It is shown below how 1-BP can meet the “ethane k_{OH} bright line” criteria on a weight basis, but experimental evidence suggests that subsequent to reaction with OH the ozone-forming

potential of 1-BP is clearly different in time than that of ethane. That is, during the early stages of ozone formation the atmospheric chemistry associated with 1-BP may accelerate ozone build-up compared to ethane, but as the peak ozone is approached and subsequently thereafter, the 1-BP chemistry actually tends to destroy ozone. Ethane chemistry is not known to destroy ozone under urban conditions. The ability of 1-BP chemistry to destroy ozone appears to be associated with the release of bromine. As noted above the presence of bromine has been linked to tropospheric ozone destruction over the Arctic and the Dead Sea^{2,3,4}.

An example compound that impacts ozone differently than ethane is acetone. Acetone easily meets the ethane k_{OH} bright-line criteria, but, due to its photolysis, acetone may show ozone-forming behavior similar in magnitude but somewhat different in character to the reactivity of ethane. Yet the EPA did grant acetone “non-reactive” status⁸, because on average the ozone-forming potential of acetone was shown to be close to that of ethane on a weight basis. For acetone⁸ “The EPA has chosen to use the weight basis rather than a mole basis for comparing results since emissions are regulated on a weight basis.” This paper presents a methodology that can be used to compare the ozone-forming potentials of unusual VOC such as 1-BP against that of ethane for conditions typical of a smog episode.

HYDROXYL RADICAL REACTIVITY

The rate constant (k_{OH}) for the hydroxyl radical reaction with the 1-bromopropane has been measured by several groups⁹⁻¹³. The first measurement⁹ was done at room temperature and pressure relative to the hydroxyl reaction with cyclohexane and produced a value of $1.18 \pm 0.3 \times 10^{-12} \text{ cm}^3$ per molecule-sec, where the uncertainty represents 2 standard deviations here and throughout this paper. Two later k_{OH} measurements^{10,11} were direct measurements over wide temperature ranges that included room temperature, but at fairly low pressures. Those two measurements were $1.14 \pm 0.12 \times 10^{-12} \text{ cm}^3$ per molecule-sec and $1.06 \pm 0.15 \times 10^{-12} \text{ cm}^3$ per molecule-sec. Recently, three more k_{OH} measurements were made.^{12,13} Those k_{OH} values were $8.7 \pm 0.4 \times 10^{-13} \text{ cm}^3$ per molecule-sec, $9.53 \pm 0.37 \times 10^{-13} \text{ cm}^3$ per molecule-sec, and a value of $1.01 \pm 0.015 \times 10^{-12} \text{ cm}^3$ per molecule-sec, which was reported¹³ but the study is not yet published. In spite of the different measurement techniques and pressures, all the k_{OH} determinations give quite similar results at room temperature. The statistically unweighted

average of the five published k_{OH} determinations is $1.04 \pm 0.07 \times 10^{-12} \text{ cm}^3$ per molecule-sec. A more precise estimate of the overall mean is a statistically weighted average using the reciprocals of the variances as weighting factors, which gives a statistically weighted k_{OH} average of $9.32 \pm 0.25 \times 10^{-13} \text{ cm}^3$ per molecule-sec. The statistically unweighted and weighted averages of the all six k_{OH} determinations are 1.04 ± 0.06 and $0.99 \pm 0.01 \times 10^{-12} \text{ cm}^3$ per molecule-sec.

The reaction rate constant for 1-BP with the hydroxyl radical can be shown to be statistically significantly less than that of ethane on a weight basis. First, it is possible to generate objective statistical representations of an existing database of measured rate constants for the reaction of the hydroxyl radical with ethane. The National Institute of Standards and Technology (NIST) maintain kinetics software with a database¹⁴ that shows some 43 studies of this reaction between 1949 and 1998. Uncertainty estimates were not provided for the majority of the studies and so have not been used for these analyses. Assuming a normal distribution, the mean value of these studies is $2.80 \times 10^{-13} \text{ cm}^3$ per molecule-second and the 95 percent confidence interval ranges from 2.61 to 2.98 (10^{-13} cm^3 per molecule-second). Of the 43 determinations two especially high values and one especially low value might be considered as outliers. Removing these three outliers reduces the mean value to $2.73 \times 10^{-13} \text{ cm}^3$ per molecule-second and the 95 percent confidence interval now ranges from 2.62 to 2.84 (10^{-13} cm^3 per molecule-second).

Two scientific committee recommendations exist^{15,16} for the ethane rate constant (k_{OH}) and these are 2.4 and 2.5 ($10^{-13} \text{ cm}^3 \text{ molec.}^{-1} \text{ sec}^{-1}$), respectively. The subjective ranges of uncertainty given by these two expert committees overlap into the “confidence intervals” objectively determined here. The NASA committee¹⁵ range is 2.18 to 2.64 ($10^{-13} \text{ cm}^3 \text{ molec.}^{-1} \text{ sec}^{-1}$), while the IUPAC committee¹⁶ range is 1.98 to 3.15 ($10^{-13} \text{ cm}^3 \text{ molec.}^{-1} \text{ sec}^{-1}$). These ranges both extend lower than the lowest 95 percent confidence ranges determined here even without the “outlier” values.

A summary of the above numbers is provided in Table 1, where the values have been converted to a weight basis appropriate for the present comparison. Conversion to per weight basis is done for this comparison by dividing the above numbers by the molecular weight of ethane,

which is 30.07 or the molecular weight of 1-bromopropane which is 123.0. The units of the k_{OH} values shown in Table 1 are 10^{-15} cm³ per molecule-second per atomic weight unit.

Table 1. Ranges of ethane and 1-BP rate constants for reaction with OH on a weight basis.

Ethane rate constants with OH	Weight-basis k_{OH}	
	Low	High
All 43 studies	8.69	9.91
Excluding 3 outliers	8.71	9.43
NASA committee	7.25	8.78
IUPAC committee	6.58	10.48
Measurements of 1-bromopropane (range)	7.07	9.59

As can be seen from Table 1, the range of actual individual measurements of the 1-bromopropane rate constant not only overlap the expert committee-determined range of uncertainty for the weight-adjusted ethane rate constant, the measurements also overlap the objectively-determined statistical 95 percent confidence intervals. Also the statistically unweighted average 1-bromopropane rate constant of 8.42 (10^{-15} weight units) using all six measurements is clearly below the objectively determined 95 percent confidence interval for the ethane reaction rate, as are the statistically weighted average (8.05) and the statistically unweighted and weighted averages excluding the unpublished value (8.46 and 7.57). As shown below, a statistical comparison shows that the rate constant for 1-bromopropane is in fact statistically significantly lower than the ethane rate constant at the 5 percent significance level.

As noted above, there have been at least six separate measurements of the rate constant for reaction of OH with 1-bromopropane. Those individual values are 8.62, 9.27, 9.59, 7.07, 7.75, and an unpublished 8.21 (10^{-15} weight units). A statistical comparison between the 43 ethane k_{OH} rate constant measurements and the six 1-bromopropane k_{OH} rate constant measurements can be made using a version of the student t test. Standard two-sample t tests for comparing means assume the two populations are both normally distributed with unknown variances that are either assumed to be equal (a pooled t test) or not assumed to be equal (e.g. a Smith-Satterthwaite¹⁷ t test). If the variances are unknown and not assumed equal, the well-known Smith-Satterthwaite t test statistic is the difference in means divided by its estimated standard

error, S . If the standard deviation of the difference in means is σ , then kS^2/σ^2 approximately has a chi-square distribution with k degrees of freedom and so the t statistic approximately has a t distribution with k degrees of freedom; the possibly non-integer value of k is found by equating the estimated variance of kS^2/σ^2 with k . In this case, the variances for the 1-bromopropane rate constant measurements are taken as known, but the variances for the ethane rate constant measurements are unknown. We therefore developed and applied a version of the Smith-Satterthwaite t test for this problem, using the same technique of matching the variance of the estimated variance of the difference between the means to the variance of a suitable multiple of a chi-square random variable. The p -values for the adapted two-sample t test for these data are shown in Table 2.

Table 2. P-values for comparing 1-bromopropane and ethane rate constants on a weight basis

Ethane	1-Bromopropane	1-BP Average	Difference of means (Ethane minus 1-BP) E-16 weight units	P-value for ethane > 1-BP (one-sided)
All	All	Unweighted	0.8798	0.0127
All	All	Weighted	1.2462	0.0001
All	Exclude unpublished value	Unweighted	0.8383	0.0154
All	Exclude unpublished value	Weighted	1.7241	0.0000
Exclude 3 outliers	All	Unweighted	0.6510	0.0240
Exclude 3 outliers	All	Weighted	1.0175	0.0000
Exclude 3 outliers	Exclude unpublished value	Unweighted	0.6095	0.0378
Exclude 3 outliers	Exclude unpublished value	Weighted	1.4953	0.0000

The tabulated differences in the mean values for the ethane and 1-bromopropane rate constants show that in every case the mean 1-bromopropane rate constant is lower than the ethane rate constant. The one-sided p-values evaluate whether the 1-bromopropane rate constant is statistically significantly lower than the ethane rate constant. For example, using all the data and an unweighted 1-bromopropane average, the p-value of 0.0127 is usually interpreted as saying that we are 98 % confident that the mean 1-bromopropane rate is lower. A p-value of 0.05 or less shows that the 1-bromopropane rate is statistically significantly lower at the usual 5 % level (i.e., 95 % confidence level). In every case, the difference is statistically significant at the 5 % level.

Statistical methods can be important for comparing rate constants to ethane. For example, the EPA used statistics in the case of acetone⁸, to argue that a reported difference of 12 percent in the reactivity of acetone over ethane “is not considered to be statistically significant, considering the standard deviation of each value.” In most comparisons with k_{OH} values there has been little need for statistics because the differences between ethane and the candidates for the non-reactive list were sufficiently far apart to be obviously different. However, for the special case of 1-bromopropane (on a weight basis), the k_{OH} values are so close that a statistical comparison is necessary. And that comparison, done several ways now, consistently shows that the k_{OH} value for 1-bromopropane is statistically significantly lower than the k_{OH} value for ethane on a weight basis. Since an EPA criteria for the non-reactive list is a k_{OH} value for the candidate VOC “equal to or less than the k_{OH} of ethane,” then 1-bromopropane passes this part of the “reactivity” test.

EXPERIMENTAL EVIDENCE

As with many halogenated VOC there are still some uncertainties in the detailed photodegradation mechanism of 1-bromopropane in the atmosphere in the presence of ozone. However, there is smog chamber experimental evidence that clearly shows 1-bromopropane to have little tendency to generate ozone (due to its low k_{OH} value) in the first place, and a noticeable ability to destroy existing ozone. In the smog-chamber study⁵ of 1-BP, 12 experiments were performed using urban surrogate mixtures of hydrocarbons, nitrogen oxides, and in 6 of the experiments substantial additions of 1-bromopropane.

There were six pairs of smog chamber experiments performed. The data from these experiments is reproduced in Figure 1 through 6. Four of the experimental comparisons were done under conditions using fairly high initial NO_x concentrations, which were intended to simulate urban areas characterized as having low ratios of VOC to NO_x. Each pair of experiments compared a base case using only a surrogate urban VOC and NO_x mixture against a repeat of the same concentrations of the urban mixture with a very large quantity of 1-bromopropane added.

Large additions of 1-BP were necessary in order to “see” significant ozone impacts, because the low k_{OH} value of 1-BP meant that very little could react during the six-hour time of the experiments. In fact, the 1-bromopropane additions were so large that the total VOC for each of the six comparisons were increased between 100 and 300 percent by weight. In spite of such large increases in total VOC the final observed ozone in three of the six comparisons was clearly less than the ozone generated in base mixture experiment. Moreover, in all three of the remaining comparisons the base ozone was rapidly rising when the experiment was ended, and in two of these the experiment with addition of 1-bromopropane ozone was seen to be rapidly decreasing. In the third case, the experiment with the addition of 1-bromopropane showed a leveling of ozone (as noted above the base experiment shows ozone rapidly increasing). Hence, it appears that had the base experiments been extended in time for even a couple of hours past the allotted six hours, then comparisons against the same experiments with additions of 1-bromopropane would always show that 1-bromopropane reduces peak ozone concentrations.

While 1-BP appears to always reduce peak ozone there is an apparent presence of some extra activity seen early in the experiments during the build-up of ozone until the ozone loss mechanism finally becomes dominate. Such early activity followed by ozone destruction is not common to typical VOC behavior as would be seen from ethane or propane for example. Some other VOC such as benzaldehyde and tolualdehyde, for example, are known to exhibit somewhat similar albeit stronger behavior. Benzaldehyde has a reaction rate constant with the hydroxyl radical that is over 13 times higher than ethane on a weight basis, yet its Maximum Incremental Reactivity (MIR) is listed¹⁸ as negative (i.e., less ozone is formed when benzaldehyde is added to the atmosphere). The experimental evidence seen for 1-BP, as

discussed here, also appears to show some negative reactivity. In particular, the ozone loss mechanism itself may always eventually lead to ozone peak reductions from 1-BP additions. That is, for ozone peaks 1-bromopropane appears to have a negative ozone-forming potential.

It is very important to note that the extra early activity observed from 1-bromopropane may be related more to bromine atoms and not to the so-called HOx radicals that are central to the chemistry paradigm that explains urban photochemical ozone formation¹⁹. The relationship between bromine atoms and HOx radicals also appears to be more complex than the relationship seen for chlorine atoms, for example. Contrary to bromine atoms, chlorine atoms readily abstract hydrogen atoms bonded to carbon leading to the same series of smog-forming radical transfer reactions as those initiated by hydroxyl radicals. For example, the reactions of ethane with hydroxyl radicals, chlorine atoms, and bromine atoms can start the same smog-forming sequence (that ends in the formation of a hydroxyl radical), but the chlorine atom reacts over two orders of magnitude faster than the hydroxyl radical, while the bromine atom reacts about six orders of magnitude slower than the hydroxyl radical. That is, the chlorine reacts more than a hundred million times faster than bromine with ethane; yet they all lead to the following generic smog-forming VOC-cycle sequence²⁰ (eq 1 through 5):



Note that the above VOC-cycle sequence leads to two NO to NO₂ conversions (which are the key reactions associated with ozone build-up) and that a hydroxyl radical is restored or generated (in the case of the halogen initiated sequences). Nevertheless, the extremely slow initial reaction of bromine effectively eliminates this type of sequence under atmospheric conditions. Hence, the presence of more bromine atoms in the system is not necessarily related

to more ozone formation in the way that more hydroxyl radicals or more chlorine atoms might be. When the smog formation reactions are “blocked” due to such low reaction rate constants, then other reactions of bromine will occur instead. One possible sequence involving bromine that leads to NO to NO₂ conversion is as follows (eq 6 and eq 7):



However, this involves the loss of an ozone molecule. Nevertheless, as ozone builds up then NO is reduced so that BrO would react in other ways, such as with itself, leading to net ozone destruction mechanisms. In an attempt to simulate the observed ozone destruction seen in the smog chamber experiments several reactions related to 1-BP chemistry were used. Nearly 60 reactions involving bromine were added to the Carbon Bond mechanism²¹, over a 65 percent increase in the number of reactions. And the experimental evidence suggests that these and perhaps other reactions involving bromine often lead to ozone destruction, especially after some ozone has formed. Modeling evidence here suggests that reaction of the bromine atom with ozone (eq. 6 here and reaction number 98 in Table 3) is the most important reaction for ozone destruction. The many other reactions involving either the production or the reaction of bromine atoms then are important for moderating or enhancing the availability of this atom to destroy ozone.

SIMULATIONS OF DATA

The modeling of smog chamber data related to specific compounds helps to either confirm the understanding of their smog-forming chemistry or to at least indicate what types of reactions might explain unusual behavior. To simulate the reported data⁵ the Carbon Bond Mechanism (version IV or CB-IV)²¹ was used for the surrogate mixtures and nitrogen oxide chemistry. As a starting point for the 1-BP chemistry and the related bromine inorganic chemistry, another mechanism²² was used with appropriate conversions of the organic species to CB-IV equivalents. Further additions to the reported²² chemistry for 1-BP have included the following:

- 1 Previously²² the ketone product stemming from the hydroxyl attack on 1-BP is treated as normal acetone. In this work bromoacetone (the expected product) was used instead. Although no quantum yield data for the photolysis of bromoacetone were available, the spectrum and cross-section data for bromoacetone²³ indicate that bromoacetone would photolyze much faster than acetone itself. A rate of photolysis for bromoacetone equal to 0.5 percent of the NO₂ photolysis was used.
- 2 Previously²² the aldehyde product stemming from the bromine atom attack on ethene and propene are assumed to be “normal” aldehydes (i.e., not containing a bromine atom). In this work, bromoacetaldehyde (BALD, the expected product for ethene) was used instead to represent these bromine-containing aldehydes. Also the bromo-containing aldehyde stemming from OH attack at the C-3 position of 1-BP was also treated as BALD, which is consistent with the approach used in CB-IV. Previously²² the bromo-containing ketone expected from the bromine atom addition to trans-2-butene was not considered.
- 3 The inclusion of BALD necessitated a photolysis reaction (which was given a higher photolysis rate than acetaldehyde by analogy to bromoacetone).
- 4 The expected product of hydroxyl attack on BALD leads to a bromine-containing PAN compound (BPAN) that was given the same rate behavior as normal PAN.
- 5 Several possible cycles have been given²⁴ (mostly involving some heterogeneous steps) to explain ozone loss due to bromine. Prominent in those discussions²⁴ on bromine atom release are relationships between N₂O₅ and/or BrONO₂ with bromine-containing compounds. Therefore, to emulate this type of behavior a gas phase reaction between N₂O₅ and HBr has been assumed here.
- 6 Some reactions were added and other adjusted slightly to conform to recommended evaluations²⁵ or previous models²⁴.
- 7 As an alternate to the assumed reaction of N₂O₅ with HBr shown here, it was found that similar behavior could be obtained using a reaction between HBr and bromo-nitrate (BrONO₂) to occur at a rate of about 3×10^{-15} cm³ per molecule-sec. This is the bromine analog of the chlorine reaction found to be key in explaining the Antarctic ozone hole²⁶.

The bromine-related reactions used are given in Table 3. The rate constants are given in cm^3 , molecule, sec. units. All photolysis constants are relative to NO_2 photolysis (i.e., k_1), and the NO_2 photolysis rate shown on Table 3 is the measured value for the environmental chamber experiments⁵. The results of the smog chamber simulations are also shown in Figures 1 through 6. In the high NO_x experiments (Figures 1 through 4) the mechanism tends to overstate (Figure 3 the least) the early rise in ozone due to 1-BP addition. However, in all cases the addition of 1-BP shows a reduction in ozone as the base peak (i.e., without 1-BP) is approached. For experimental cases where this was not actually observed (due to termination of the base experiment) the model was continued and, indeed the 1-BP addition always resulted in less peak ozone.

Even though the early ozone build-up tended to be overstated, the mechanism used here also tended to understate the ozone destruction from 1-BP. That is, the down-slope in observed ozone was always steeper than in the model. In the five experiments where the data show definite ozone destruction, the simulations understate that destruction by an average of 65 percent. Although the mechanism and simulations presented here do show lower peak ozone, the mechanism does tend to overstate the reactivity of 1-bromopropane in the early ozone build-up phase and in the ozone destruction phase. Another issue that is inconsequential to a reactivity determination is the presence in the simulations of a consistent understatement of ozone for the low NO_x experiments shown in Figures 5 and 6. This circumstance was also observed to some extent previously²².

As a further confirmation of the low reactivity of 1-bromopropane, the simulated reactivity is low even for the parts of the simulations where the initial rate of ozone formation is overstated. This overstated simulated ozone is seen during the early period of smog development under high NO_x conditions. This extra reactivity was estimated to be comparable to acetone (another compound already declared non-reactive by the U.S. EPA⁸).

To show comparisons of 1-BP with equal weight additions of ethane and acetone, simulations are also shown in Figures 1 through 6. The observed ozone data from 1-BP can be compared to the simulated ozone from ethane and acetone additions. In all six cases the peak ozone values from the 1-BP data were always lower than the peak simulated ozone values from either the ethane or the acetone addition. However, there were periods during ozone build-up when the ozone data from 1-BP were higher than the simulated ozone values from either ethane or

acetone additions. As to how ethane and 1-BP might compare under more realistic conditions a photochemical grid model was deemed more appropriate.

PHOTOCHEMICAL GRID MODEL SIMULATIONS

Because 1-BP is used to replace CFC solvents, solvent emissions locations and diurnal profiles were chosen to simulate either ethane or 1-BP additions. Because 1-BP and ethane are so low in reactivity very large additions (500 tons per day) are necessary to “see” and impact, which is similar to the reason why such large additions of 1-BP were needed in the smog chamber experiments. For a test base an often-used simulation for the South Coast Air Basin was chosen. This simulation is of a well-characterized episode that occurred during 26-28 August 1987. The input files for this base case were part of the 1997 Air Quality Management Plan submitted by the South Coast Air Quality Management District²⁷. To simulate solvent usage the 500 ton per day additions were tied to the non-mobile emissions of toluene (i.e. Carbon Bond species TOL).

The total simulated time for this episode is approximately 2.3 days. Since very little ethane or 1-BP would react during such a timeframe and not all of the basin is emptied each day, it is safe to say that either compound would accumulate somewhat over the course of the episode. In spite of such large additions ethane and 1-BP the simulated increases in peak ozone for this episode was only 1.7 ppb for ethane and 0.9 ppb for 1-BP. As yet another measure of the low reactivity of these two species, it should be noted that a 500 ton per day addition represents about a 25 percent increase in the total VOC emissions inventory. The base case 1-hour ozone was simulated to be 188.7 ppb.

For the 8-hour measure of peak ozone, 1-BP exhibited a negative effect. The base case 8-hour ozone peak was 170.4 ppb; the simulated 500 ton per day addition of 1-BP reduced this by 0.9 ppb, while the simulated ethane addition increased peak 8-hour ozone by 2.0 ppb. Hence, it appears that 1-BP can not only give peak ozone values less than ethane (as seen for the 1-hour standard measure), there may be cases where the ozone destruction part of the 1-BP chemistry dominates enough to show a net negative reactivity (as seen for the measure of ozone peak that relates to a potential 8-hour standard).

Since the base inventory will be different in 2010 compared to 1987, it is also useful to see if the change in base emissions will increase or decrease the impacts of 1-BP. The future 1-hour “attainment” inventory of the 1997 Air Quality Management Plan²⁷ was therefore used to repeat the above 500 ton impact simulations. With the future emissions the ability of 1-BP to reduce peak ozone was stronger, while ethane showed higher increases in ozone. That is, the comparison of 1-BP to ethane shows a significant trend toward even less ozone from 1-BP compared to ethane as the base emissions are reduced. For 2010 the base case 1-hour ozone was simulated to be 112.3 ppb; the simulated 500 ton per day addition of 1-BP reduced this by 1.7 ppb, while the simulated ethane addition increased peak 1-hour ozone by 3.7 ppb. For the 8-hour ozone peaks the 2010 inventory reduced the maximum to 103.0 ppb; the simulated 500 ton per day addition of 1-BP reduced this by 0.9 ppb, while the simulated ethane addition increased peak 8-hour ozone by 4.3 ppb. Figures 7 and 8 show the simulated 2010 base 8-hour ozone values and the difference in local 8-hour ozone peak concentrations between the ethane and 1-BP additions. Although the VOC to NO_x ratio remained similar between the two years, the reduced emissions apparently enhance the ability of 1-BP to reduce peak ozone. The total NO_x emissions were reduced 61 percent between the 1987 and 2010 inventories; the VOC were reduced 65 percent.

CONCLUSIONS AND RECOMMENDATIONS

While the exact details of the atmospheric chemistry of 1-BP remain uncertain, there can be little doubt that 1-BP will have minimal impact on urban smog. This minimal impact appears to be less than ethane, the compound the U.S. EPA has set as the standard for “negligible” reactivity and eligible for non-reactive VOC status. The approach taken here was first to show that the reaction rate constant for the hydroxyl radical reaction 1-bromopropane is lower than the ethane rate constant on a weight basis to a statistical confidence of 95 percent certainty. A low rate constant with this radical guarantees that 1-BP will have a low impact on smog formation because there appears to be no other way for 1-BP to react in the atmosphere and such a low rate means that only a small fraction of 1-BP can react per day. Second, a “place holder” reaction set was developed to approximate the effects of 1-BP chemistry seen in smog chamber experiments. Third, potential smog chamber experiments with ethane and acetone were simulated for comparison with the 1-BP data to show that 1-BP is close in reactivity to

these low-reactive VOC. Fourth, the “place holder” reactions were added to the Carbon Bond IV reactions used in the photochemical Urban Airshed Model that is used to simulate control strategies and air management plans. Simulations of an often-used smog episode with 500 ton per day additions of either ethane or 1-BP showed that peak ozone tended to be higher from ethane than from 1-BP. Using the 8-hour ozone peak as a measure of impact, the 1-BP addition actually showed less simulated ozone than the base case without any additions. That is, for this 8-hour metric, 1-BP exhibited a negative reactivity. Fifth, by using base emissions inventories for both the observed 1987 episode and the predicted attainment of the ozone 1-hour standard in 2010, the trend is for 1-BP emissions to show even more negative reactivity in the future. Moreover, this trend shows more favorable comparisons to ethane for 1-BP as the base emissions are reduced as part of ozone abatement strategies.

Follow-on studies might be made to find better simulations of the 1-BP chemistry and to determine more details of individual reactions used in the “place holder” scheme used here. For example, a reaction between N_2O_5 and HBr was assumed here, but no rate data is available for such a gas phase reaction or the potential for heterogeneous effects that might mimic such a reaction. Also several photolysis rates were used based on published values²⁸ relative to NO_2 . The actual photolysis rates in the smog chamber experiments or in the atmosphere may be somewhat different than used here. While too late to fully evaluate for this study, measurements¹³ of the product distribution from the OH attack on 1-BP are similar but different from those used here based on earlier estimates.²² The use of the measured product distribution did help bring the smog chamber simulations closer to the observed data.

REFERENCES

1. Dimitriadis, B. Photochemical Smog and Solvents; *Metal Finishing* 1997, May, 55-59.
2. Foster, K.L.; Plastring, R.A.; Bottenheim, J.W.; Shepson, P.B.; Finlayson-Pitts, B.J.; Spicer, C.W. The Role of Br_2 and $BrCl$ in Surface Ozone Destruction at Polar Sunrise; *Science* 2001, 291, 471-474.

3. Matveev, V.; Peleg M.; Rosen D.; Tov-Alper D.S.; Hebestreit K.; Stutz J.; Platt U.; Blake D.; Luria, M. Bromine oxide – ozone interaction over the Dead Sea; *Journal of Geophysical Research* 2001, 106, 10,375-10,387.
4. Stutz, J.; Hebestreit, K.; Alicke, B.; Platt, U. Chemistry of Halogen Oxides in the Troposphere: Comparison of Model Calculations with Recent Field Data; *Journal of Atmospheric Chemistry* 1999, 34, 65-85.
5. Carter, W.P.L.; Luo, D.; Malkina, I.L. Investigation of the Atmospheric Ozone Formation Potential of Selected Alkyl Bromides; Final Report to Albemarle Corporation 1997, College of Engineering Center of Environmental Research and Technology, University of California, Riverside, available at <http://www.cert.ucr.edu/~carter/absts.htm#alkbr>.
6. Dimitriadis, B. Scientific Basis for the VOC Reactivity Issues Raised by Section 183 (e) of the Clean Air Act Amendments of 1990; *Journal of the Air & Waste Management Association*, 1996, 46, 963-970. Also section 40 of the Code of Federal Regulations [CFR] Part 51.100.
7. Prinn, R. G.; Weiss, R. F.; Miller, B. R.; Huang, J. Atmospheric Trends and Lifetime of CH₃CCl₃ and Global OH Concentrations; *Science* 1995, 270, 187-192.
8. Federal Register, 60 **FR** 31633.
9. Donaghy, T.; Shanahan, I.; Hande, M.; Fitzpatrick, S. Rate Constants and Atmospheric Lifetimes for the Reactions of OH Radicals and Cl Atoms with Haloalkanes; *International Journal of Chemical Kinetics* 1993, 25, 273-284.
10. Teton, S.; El Boudali, A.; Mellouki, A. Rate constants for the reactions of OH radicals with 1- and 2-bromopropane; *Journal of Chemical Physics* 1996, 93, 274-282.

11. Nelson, D.D., Jr.; Wormhoudt, J.C.; Zahniser, M.S.; Kolb, C.E.; Ko, M.K.W.; Weisenstein, D.K. OH reaction kinetics and atmospheric impact of 1-bromopropane; *Journal of Physical Chemistry* 1997, A:101, 4987-4990.
12. Herndon, S.C.; Gierczak T.; Talukdar, R.K.; and Ravishankara, A.R. Kinetics of the reactions of OH with several alkyl halides; *Physical Chemistry Chemical Physics* 2001, 3, 4529-4535.
13. Gilles, M.K.; Burkholder, J.B.; Gierczak J.B.; Marshall P.; and Ravishankara, A.R. Rate Coefficient and Product Branching Measurements for the Reaction of OH + Bromopropane from 230 to 360K; *Journal of Physical Chemistry* 2002, 106, 5358-5366.
14. National Institute of Standards and Technology (NIST) Kinetics Database 17, available at <http://kinetics.nist.gov/index.php>.
15. DeMore, W.B.; Sander, S.P.; Howard, C.J.; Ravishankara, A.R.; Golden, D.M.; Kolb, C.E.; Hampson, R.F.; Kurylo, M.J.; Molina, M.J. Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling: Evaluation Number 12; JPL Publication 97-4 1997, NASA.
16. Atkinson, R.; Baulch, D.L.; Cox, R.A.; Hampson, R.F., Jr.; Kerr, J.A.; Rossi, M.J.; Troe, J. Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry, Organic Species: Supplement VII, IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry; *Journal of Physical and Chemical Reference Data* 1999, 28, 191-393.
17. Satterthwaite, F.W. (1946), "An Approximate Distribution of Estimates of Variance Components," *Biometrics Bulletin*, 2, 110 -114.
18. Carter, W.P.L. The SAPRC-99 Chemical Mechanism and Updated VOC Reactivity Scales; Final Report to the California Air Resources Board 2000, College of Engineering Center of

Environmental Research and Technology, University of California, Riverside, available at <http://www.cert.ucr.edu/~carter/reactdat.htm>.

19. Johnston, H.S. Atmospheric Ozone; *Annual Reviews of Physical Chemistry* 1992, 43, 1
20. Whitten, G.Z. The Chemistry of Smog Formation: A Review of Current Knowledge; *Environment International* 1983, 9, 447-463.
21. Gery, M.W.; Whitten, G.Z.; Killus, J.P.; Dodge, M.C. A Photochemical Kinetics Mechanism for Urban and Regional Computer Modeling; *Journal of Geophysical Research* 1989, 94, 12,925-12,956.
22. Carter, W.P.L.; Tuazon, E.C. Atmospheric Chemistry of Bromine-Containing Compounds; Final Report to the Brominated Solvents Consortium 2000, College of Engineering Center of Environmental Research and Technology, University of California, Riverside, available at <http://www.cert.ucr.edu/~carter/absts.htm#brreport>.
23. Kash, P.W.; Waschewsky, G.C.G.; Morss, R.E.; Butler, L.J.; Francis, M.M. Competing C-Br and C-C bond fission following $^1[n(O), \pi^*(C=O)]$ excitation in bromoacetone: Conformation dependence of nonadiabaticity at a conical intersection; *Journal of Chemical Physics* 1994, 100, 3463-3475.
24. Moldanova, J.; Ljungstrom, E. Sea-salt aerosol chemistry in coastal areas: A model study; *Journal of Geophysical Research* 2001, 106, 1271-1296.
25. Atkinson, R.; Baulch, D.L.; Cox, R.A.; Hampson, R.F., Jr.; Kerr, J.A.; Rossi, M.J.; Troe, J. Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry, Organic Species: Supplement VIII, Halogen Species, IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry; *Journal of Physical and Chemical Reference Data* 2000, 29, 167-266.
26. Abbatt, J.P.D.; Molina, M.J. Interaction of HCl Vapor with Water Ice: Implications for the Stratosphere; *Journal of Geophysical Research* 1992, 97, 15819-15826.

27. Air Quality Management Plan (AQMP) for 1997 (<http://www.aqmd.gov/aqmp/97aqmp>)

28. Jacobson, Mark Z. *Fundamentals of Atmospheric Modeling* 1999, Cambridge University Press, UK.

Figure Captions

Figure 1. DTC-433 5.5 ppm Mini-Surrogate + 3 ppm 1-BP + 0.37 ppm NO_x

Figure 2. DTC-421 5.8 ppm Mini-Surrogate + 4.8 ppm 1-BP + 0.37 ppm NO_x

Figure 3. DTC-423 5.2 ppm Full Surrogate + 2.1 ppm 1-BP + 0.30 ppm NO_x

Figure 4. DTC-427 4.7 ppm Full Surrogate + 5.4 ppm 1-BP + 0.29 ppm NO_x

Figure 5. DTC-424 4.9 ppm Full Surrogate + 2.1 ppm 1-BP + 0.12 ppm (Low) NO_x

Figure 6. DTC-428 4.8 ppm Full Surrogate + 5.7 ppm 1-BP + 0.11 ppm (Low) NO_x

Figure 7. Base Case 2010 UAM Simulation, 8-hour local peak ozone (ppb).

Figure 8. 2010 UAM Simulation Differences (500 tons 1-BP minus 500 tons ethane), 8-hour local peak ozone (ppb).

Figure 1. DTC-433
Mini-Surrogate + 3ppm 1-BP

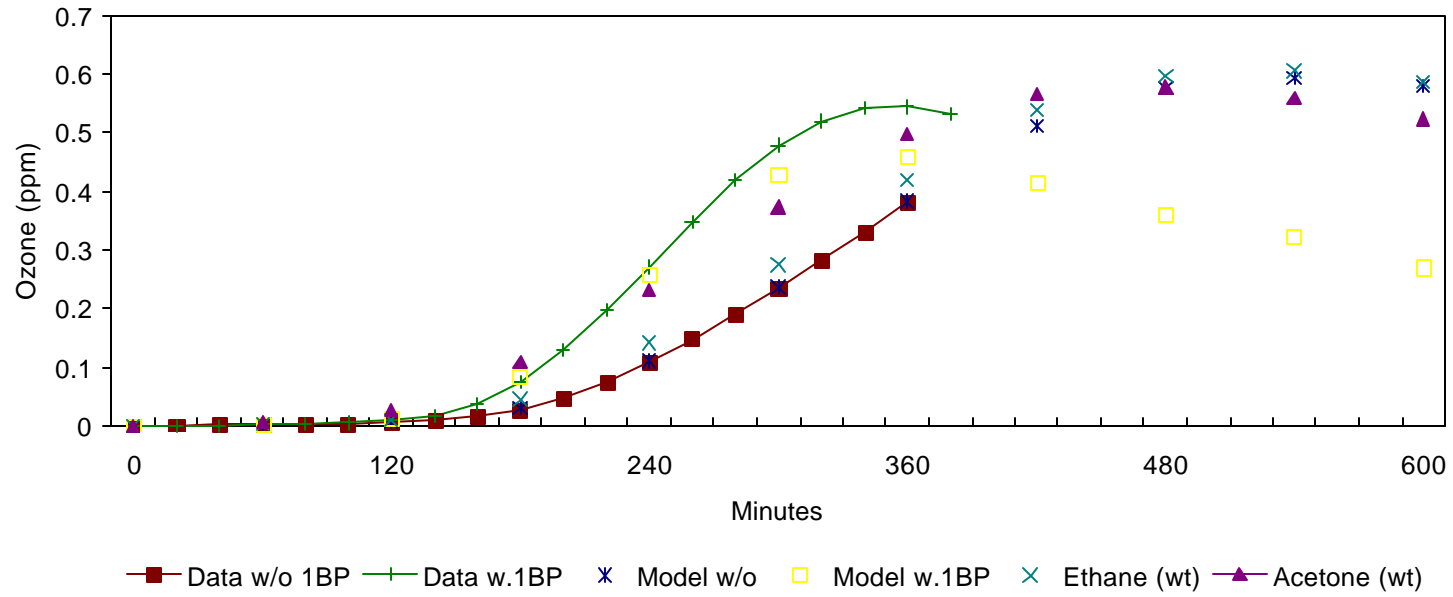


Figure 3. DTC-423
Full Surrogate + 2ppm 1-BP

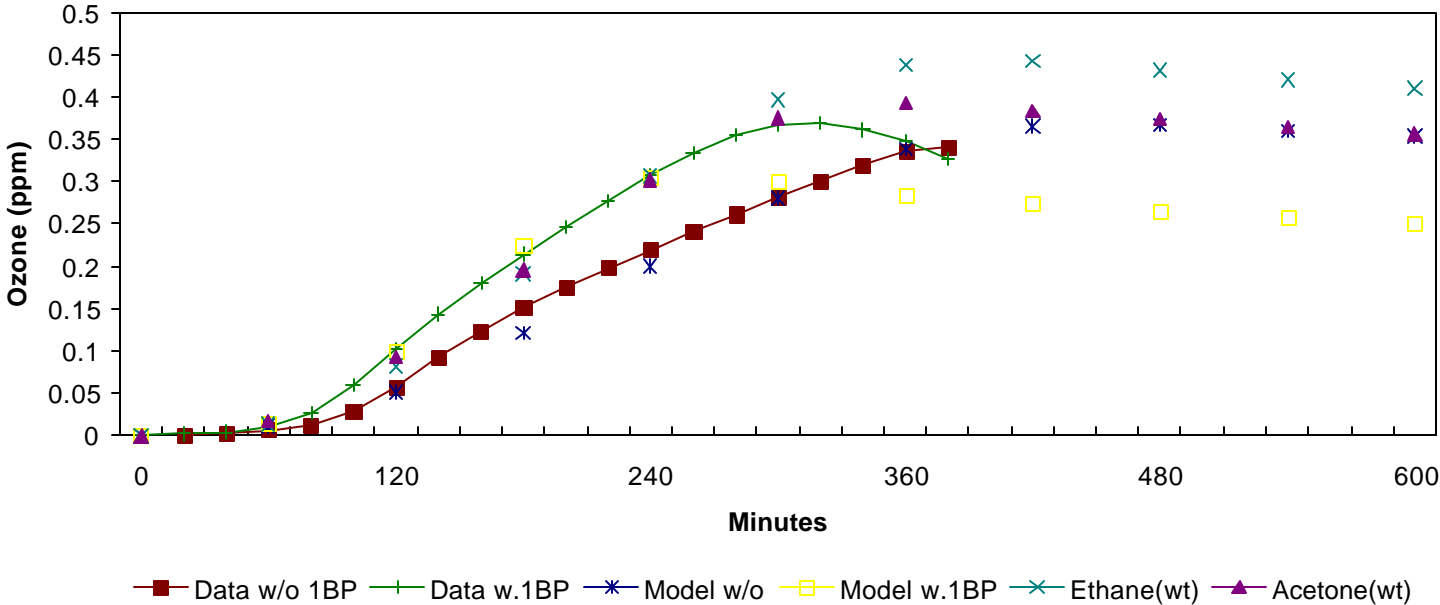


Figure 4. DTC-427
Full Surrogate + 5ppm 1-BP

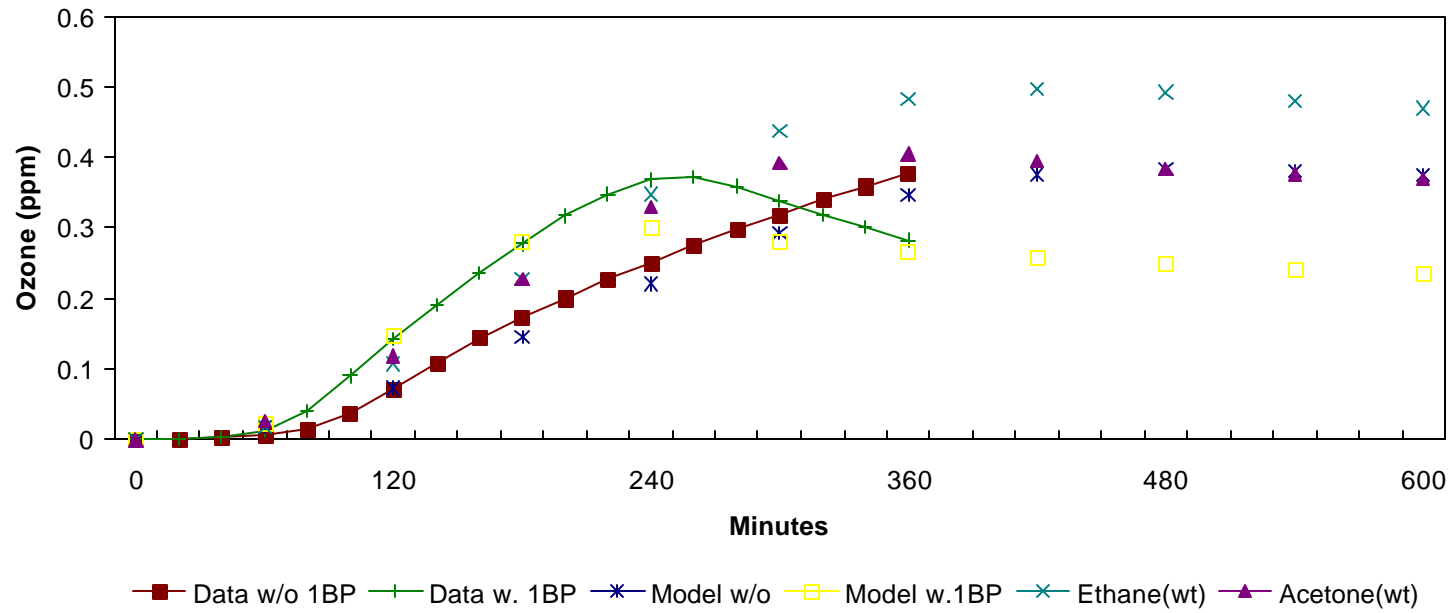


Figure 5. DTC-424
Low NOx Full Surrogate + 2ppm 1-BP

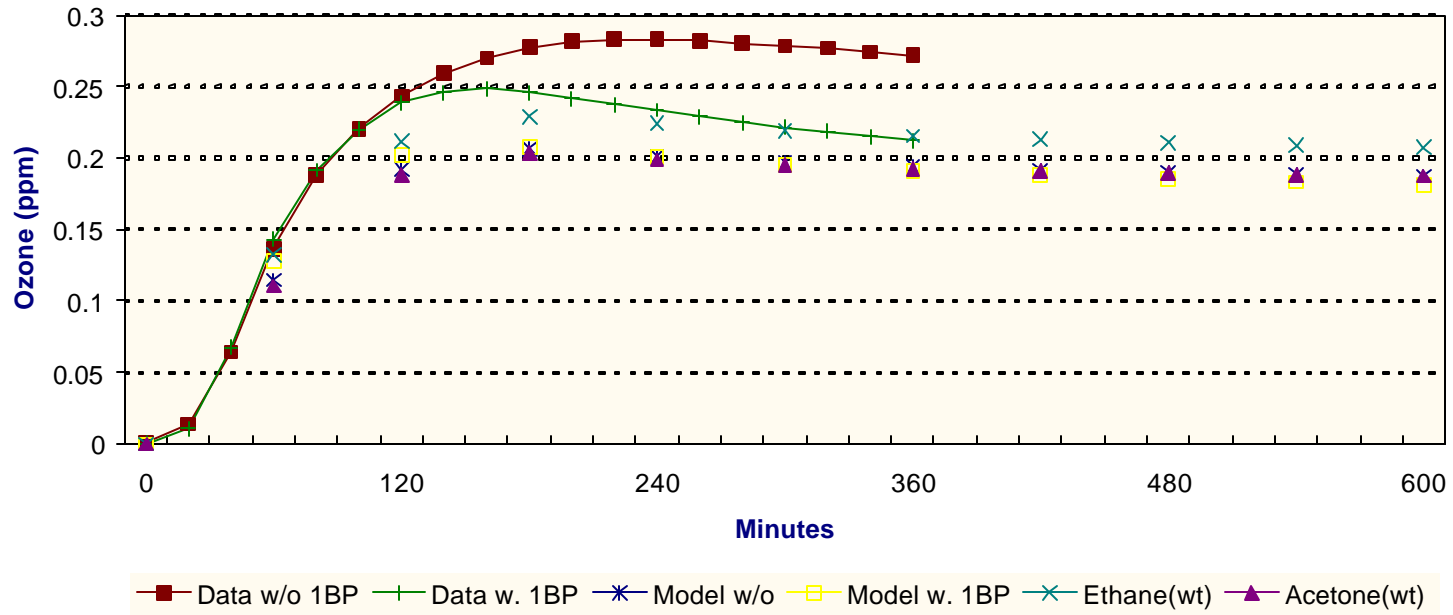
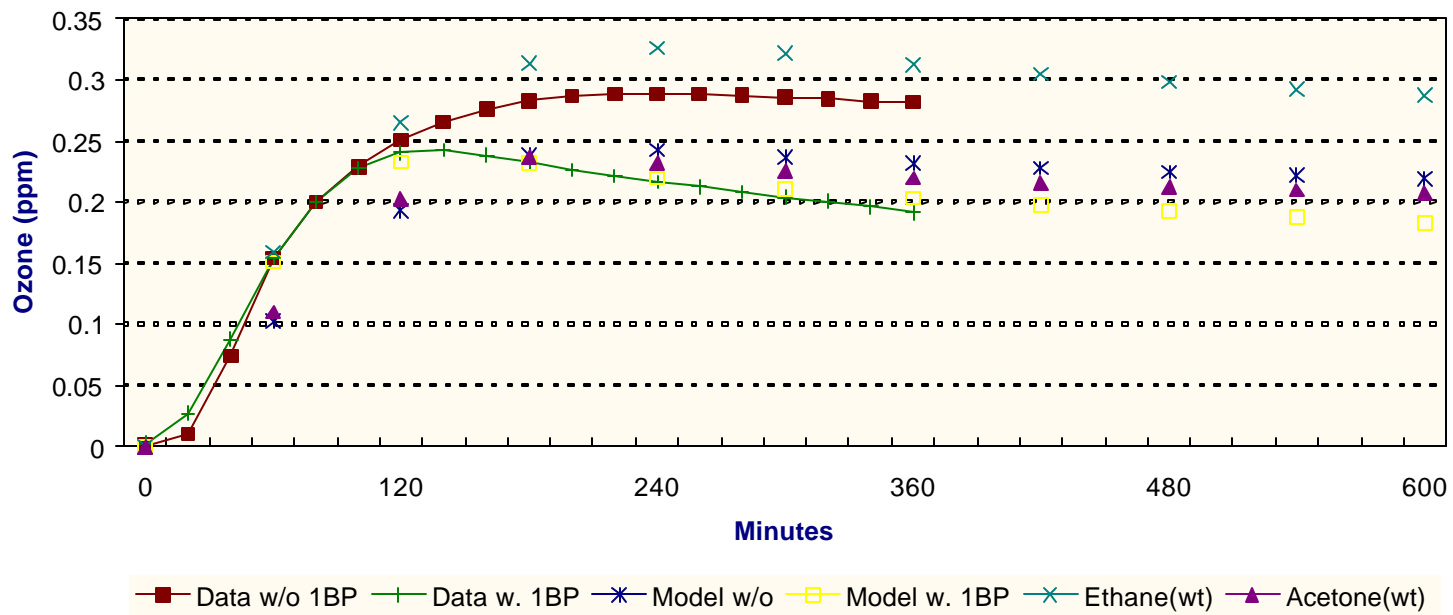


Figure 6. DTC-428
Low NOx Full Surrogate + 6ppm 1-BP



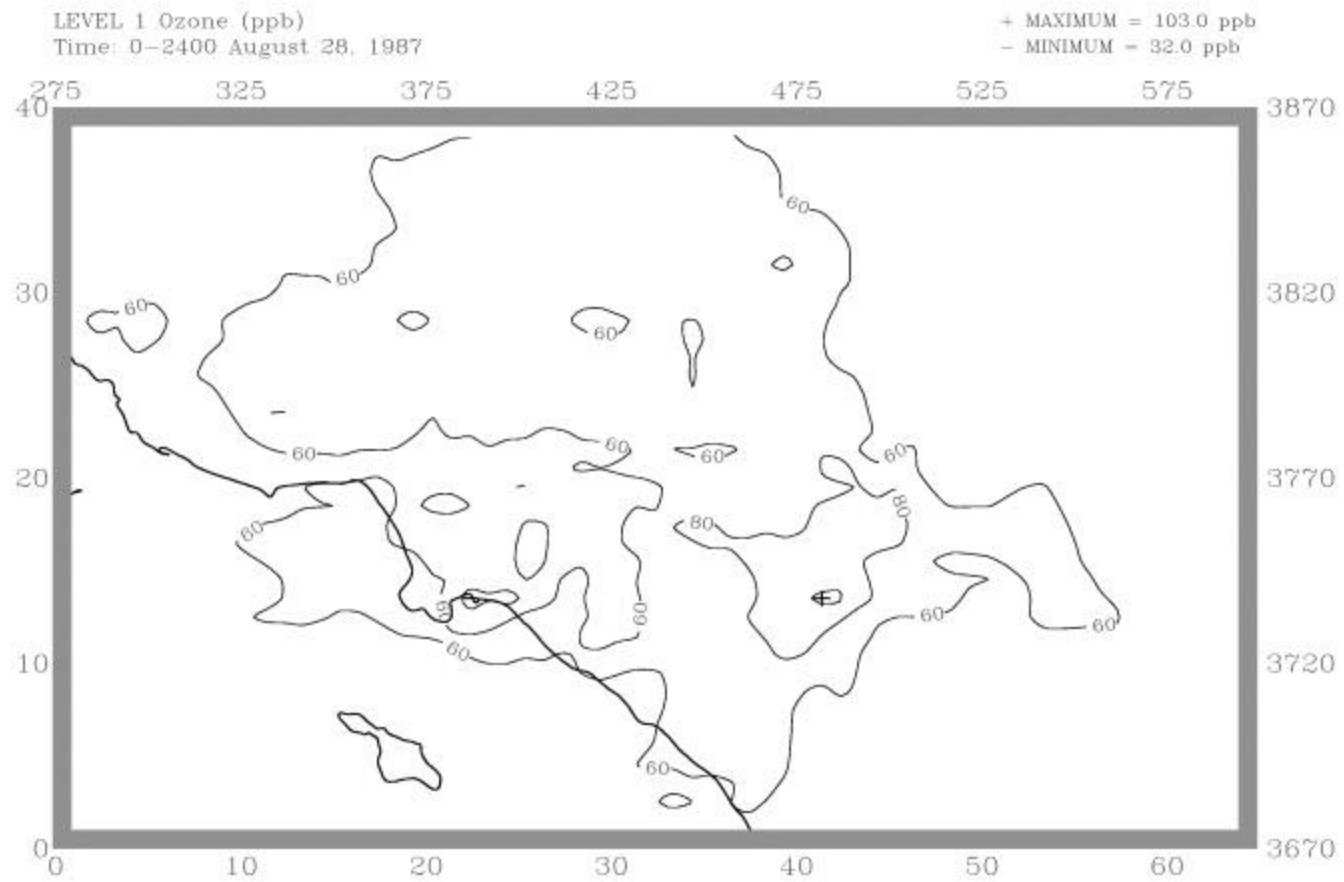


Figure 7. Base Case 2010 UAM Simulation, 8-hour local peak ozone (ppb).

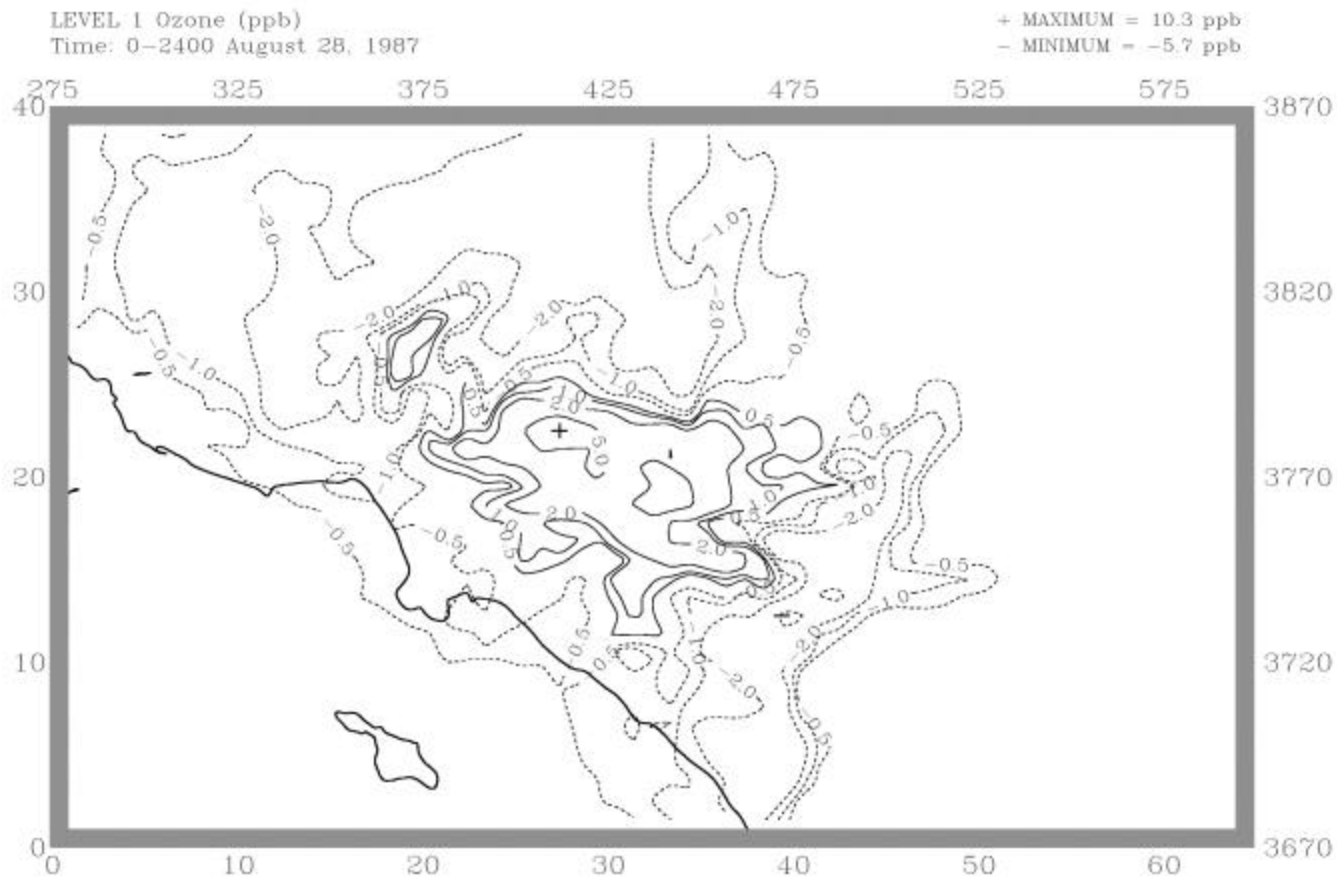


Figure 8. 2010 UAM Simulation Differences (500 tons 1-BP minus 500 tons ethane), 8-hour local peak ozone (ppb).