

OZONE REACTIVITY ANALYSIS OF EMISSIONS FROM
MOTOR VEHICLES

by

William P. L. Carter
Air Pollution Research Center
University of California
Riverside, CA 92512

Prepared for the Western Liquid Gas Association

July 11, 1989

SUMMARY

This report describes a method for analyzing the impacts on ozone formation of emissions of CO and volatile organic compounds (VOCs) from motor vehicles, given the results of detailed speciated analyses of exhaust and evaporative emissions. The analysis is based on estimating maximum amounts of additional ozone formed caused by CO and VOC emissions from the motor vehicles in idealized scenarios representing photochemical smog formation. The ozone impacts are given as grams of ozone formed per gram exhaust or evaporative VOC emitted, and as grams of ozone formed per vehicle mile traveled. The method is illustrated using results of analyses recently carried out by the California Air Resources Board of emissions from several motor vehicles utilizing gasoline and various alternative fuels. Contributions of the various individual compounds to the overall reactivity of the emissions are calculated, and the relative reactivities of the emissions from these vehicles calculated in this work are compared with results of analyses based only on considerations of the OH radical rate constants of the individual compounds. General issues involved in the estimation of ozone reactivities of VOC emissions from motor vehicles and other sources are briefly discussed.

INTRODUCTION

Volatile organic compounds (VOCs), when emitted into the atmosphere, react to contribute to the photochemical formation of ozone, a major air quality problem in many urban areas. Motor vehicles constitute a major source of these emissions. Various approaches can be employed to reduce the contribution of motor vehicle emissions to ozone formation. One obvious approach is to reduce the total amount of vehicle miles traveled in ozone non-attainment areas. Another approach is to encourage or mandate use of "low-emission" motor vehicles, whose emissions cause less ozone formation per mile traveled than do present vehicles. This could involve either reducing the total amounts of VOC emitted, or reducing the reactivity of these emissions with respect to ozone formation. For example, modifications to conventionally-fueled vehicles has already resulted in reductions of their total VOC emissions, and use of alternative fuels such as methanol is being considered for further reducing ozone impacts by reducing emission reactivity. Methanol is not the only alternative fuel which might lead to air quality benefits; more widespread use of fuels such as hydrogen, methane, propane, or ethanol is also being proposed as a means to reduce ozone impacts of motor vehicle emissions. In order to assess the relative benefits of these alternative approaches, and to develop appropriate regulations and standards to encourage or mandate use of low-emissions vehicles, some means is necessary to quantify ozone impacts of vehicular VOC emissions which take both quantity and reactivity into account.

In the past, the regulations and standards for VOC emissions from vehicles has been based only on total amounts of VOC emitted. This is not useful for assessing use of alternative fuels, since it does not take differences in reactivity into account. Alternatively, detailed airshed model simulations can be used to assess the effects of specific fuel substitution scenarios on selected air pollution episodes. An example of this is the recent Carnegie-Mellon study of impacts of methanol fuel substitution in the California South Coast Air Basin (Russell et al. 1989). While this latter approach can probably give us the best available estimates of specific fuel substitution scenarios under specific sets of conditions (though such calculations are not without significant uncertainties), this is an extremely expensive procedure, and it is not practical for assessing the wide variety of options and approaches which might be employed. The results of such an assessment may be no more applicable for conditions of other airsheds, or even of other episodes within the same airshed, than results of much more simple calculations. What is required is a simpler and more generally applicable procedure for estimating ozone impacts of VOC emissions from vehicles, which takes reactivity considerations into account.

The procedure described in this report for assessing ozone impacts of VOC emissions is also based on airshed model calculations, but of a much more idealized type. Rather than estimating impacts of VOC emissions on ozone formation in specific episodes (which are difficult to estimate because they are highly dependent on the specific conditions of the episodes and in most cases require highly complex multi-cell grid models for accurate representation), the procedure is based on estimating the maximum likely

impact of the VOC emissions on ozone. In other words, the reactivity of a VOC (or of the mixture of VOC's emitted from a particular type of vehicle) is assessed not in terms of how much ozone it forms in any particular episode, but in terms of the maximum amount of ozone it could possibly form when emitted in the atmosphere, i.e., on its maximum "potential" for ozone formation. This is an appropriate criterion to use for regulatory purposes, since conditions where VOC reactivities are the highest are by definition those where VOC control is the most effective control strategies for reducing ozone formation. Considerations involved in the use of maximum reactivity as a basis for deriving a reactivity scale are discussed in more detail elsewhere, where it has been proposed as a basis for deriving reactivity-adjusted emissions charges for solvent species (Weir et al. 1988, Carter 1989a).

The maximum reactivity of VOCs can be estimated by calculating reactivities for a variety of airshed conditions, and basing the assessment on those conditions where VOCs have the highest reactivities, i.e., where emissions of VOCs have the greatest effect on ozone formation. This is a simpler problem than estimating reactivities for a specific set of conditions, since idealized model scenarios are sufficient for this purpose. However, this approach requires knowledge or estimates of the atmospheric reaction mechanisms of each of the many types of emitted VOCs. It also requires use of a wide variety of model scenarios, to assure that the conditions where VOCs have maximum reactivity are represented. An alternative approach is to make separate estimates of (1) the maximum fraction of an emitted VOC which undergoes chemical reaction in an urban photochemical pollution episode, and (2) the maximum amount of ozone formation caused by the reaction of a given amount of a VOC. The former quantity can be estimated given a knowledge of the rates of reaction of the VOC in the atmosphere, and the latter can be estimated based on calculations of maximum reactivity for chemically similar compounds. These two quantities can then be combined to obtain an estimate of the maximum amount of ozone formed due to the emissions of a given amount of the VOC, i.e., its maximum ozone formation reactivity.

The use of the maximum reactivity scale on analyzing ozone impacts for specific types of motor vehicles is illustrated using the results of a detailed analysis reported by the California ARB on emissions from several vehicles using a variety of fuels (ARB 1989). Exhaust and (where applicable) evaporative emissions were reported for vehicles using a standard gasoline ("Indolene"), methanol and ethanol blends, neat methanol, condensed natural gas (CNG), and liquified propane gas (LPG). It should be emphasized that these results are being used for illustrative purposes only, since only a limited number of vehicles were tested and no claim was made by the ARB that these tests represent anything more than emissions from just those particular vehicles at the time these measurements were carried out. Therefore, no conclusions should be directly drawn from this report concerning probable air quality impacts resulting from future use of these various types of fuels. However, the results of these tests are useful for illustrating how maximum reactivity estimates can be applied for assessing maximum ozone impacts resulting from use of different types of fuels and motor vehicles, given the results of detailed speciated analyses of VOC emissions from such vehicles.

METHODS

DERIVATION OF MAXIMUM OZONE REACTIVITIES

The reactivity of a VOC with respect to ozone formation is measured by its "incremental reactivity". This is defined as the change in ozone caused by the addition of the VOC to a particular polluted airshed of interest (referred to as the "pollution scenario"), divided by the amount of VOC added.

$$\text{Incremental Reactivity of a VOC} = \frac{\text{Ozone Formed in Pollution Scenario with VOC Added to Emissions (Test Case)} - \text{Ozone Formed in an Idealized Pollution Scenario (Base Case)}}{\text{Amount of VOC Added to Emissions in Test Case}} \quad (\text{I})$$

If the atmospheric chemical reaction mechanism for a VOC is known or can be estimated, its incremental reactivity for the conditions of a specific pollution scenario can be estimated by carrying out model calculations of amounts of additional ozone formation caused by adding the VOC to the emissions. Although direct calculations of reactivity can be carried out for a variety of compounds, it is not practical to use this method to calculate maximum reactivities for all of the many individual compounds which may be present in solvent or exhaust emissions. Instead, in the previous study of solvent reactivities (Weir et al. 1988, Carter, 1989a), methods were developed for making separate estimates of the two major components of incremental reactivity, and then combined these to obtain maximum reactivity estimates. This approach is employed this study as well.

For the purpose of these estimates, incremental reactivity is considered as a product of two factors, which are designated as the "kinetic" and the "mechanistic" reactivities. The kinetic reactivity is the fraction of the emitted VOC which reacts

$$\text{Kinetic Reactivity} = \text{Fraction Reacted} = \frac{\text{VOC Reacted}}{\text{VOC Emitted}} ; \quad (\text{II})$$

the mechanistic reactivity is the amount of ozone formed relative to the amount of VOC which reacts

$$\text{Mechanistic Reactivity} = \frac{\text{Ozone Formed}}{\text{VOC Reacted}} ; \quad (\text{III})$$

and the product of these two quantities give the overall incremental reactivity.

$$\begin{array}{rclcl}
 \text{Incremental} & & \text{Kinetic} & & \text{Mechanistic} \\
 \text{Reactivity} & = & \text{Reactivity} & \times & \text{Reactivity} & \text{(IV)} \\
 \\
 \left(\frac{\text{Ozone Formed}}{\text{VOC Emitted}} \right) & = & \left(\frac{\text{VOC Reacted}}{\text{VOC Emitted}} \right) & \times & \left(\frac{\text{Ozone Formed}}{\text{VOC Reacted}} \right)
 \end{array}$$

These two components of incremental reactivity are more straightforward to estimate than overall incremental reactivity, and thus provide a basis for making reactivity estimates for VOCs whose atmospheric reactions are not represented in the chemical mechanisms used in current airshed models.

The estimation of these components of incremental reactivity are based on results of direct calculations of reactivities of representative compounds for a variety of idealized pollution scenarios. The chemical mechanism used for the base case emissions and for the VOCs whose reactivities were calculated is the latest version of the detailed SAPRC mechanism (Carter 1989b), which is a slightly updated version of the mechanism (Carter 1988) used in the previous study of solvent reactivity (Weir et al. 1988, Carter 1989a). The specific pollution scenarios employed have been described in detail elsewhere (Weir et al. 1988), and are briefly summarized in the following section. Following that, the methods for estimating maximum kinetic and mechanistic reactivities are discussed.

POLLUTION SCENARIOS USED FOR MAXIMUM REACTIVITY ESTIMATES

Incremental reactivity calculations were carried out for pollution scenarios including three different representations of physical aspects such as emissions schedules, dilution, etc., two different representations of base case reactive organic gas (ROG) emissions, and with the ROG/NOx ratio varied from 4 to 40. The model formulation are based on the "box model" representation such as employed in city-specific EKMA calculations, but employed dynamic injection of pollutants, time-varying inversion heights, and time-varying rates of photolysis reactions (Carter and Atkinson 1989, Weir et al. 1988). The three types of representations of physical aspects of the pollution scenarios employed in this study are as follows:

- "EKMA-1", a one-day simulation using standard city-specific EKMA inputs recommended by Gipson and Freas (1983) for use in Regulatory Impact Analyses for low dilution regions;
- "EKMA-3", a one-day simulation using standard city-specific EKMA inputs recommended by Gipson and Freas (1983) for use in Regulatory Impact Analyses for high dilution regions; and
- "Multi-Day", a two-day simulation with emissions on both days, with significant carry-over of pollutants from day 1 to day 2. The extent of dilution and the amounts of ozone formed was similar to that for the EKMA-1 scenarios.

The two surrogate mixtures used to represent base case ROG emissions in the pollution scenarios were:

- "Surrogate-A", a mixture of compounds derived based on EPA-recommended defaults for use in EKMA model calculations (EPA, 1984), which in turn is based on analyses of air quality data; and
- "Surrogate-E", a mixture of representative compounds and lumped model species derived (Carter 1988) to represent the 1983 California ARB inventory of total emissions into the California South Coast Air Basin (Croes and Allen, 1988).

The ozone yields calculated for the EKMA-1 and Multi-Day scenarios for a given ROG/NOx ratio and base case ROG surrogate were generally similar, with maximum yields being approximately 0.25 ppm at ROG/NOx ratios of 8-12. Because of the high dilution, the maximum ozone formed in the EKMA-3 do not exceed the Federal standard of 0.12. However, the maximum mechanistic reactivities for the VOCs calculated for the EKMA-3 scenarios were not significantly different from those calculated for the lower dilution scenarios, though they occurred at lower ROG/NOx ratios (Weir et al. 1988, Carter and Atkinson 1989).

The emissions-based Surrogate "E" is significantly lower in aldehydes and and somewhat lower in aromatics than the EKMA default, air quality-based Surrogate "A", and its use gives lower calculated maximum ozone yields at low ROG/NOx ratios. Scenarios using Surrogate "E" also tend to have higher maximum reactivities for most VOC's, particularly those which tend to involve radical sources in their mechanisms (Weir et al. 1988).

Therefore, most of the maximum mechanistic reactivity estimates given below are based on results of calculations using this surrogate.

ESTIMATES OF MAXIMUM KINETIC REACTIVITIES

The Kinetic Reactivity of VOC's, i.e., the fraction of emitted VOC's which react, depends on how rapidly the VOC reacts in the atmosphere, but not on the other aspects of their reaction mechanism. For most types of emitted VOC's, reaction with hydroxyl radicals is the only significant process which causes them to react in the atmosphere. Thus, for those compounds, the kinetic reactivity depends only on the rate constant for the reaction of the compound with OH radicals, and the overall level of OH radicals in the pollution scenarios. In those cases, the kinetic reactivity can be approximated by the following empirical relation:

$$\text{Kinetic Reactivity} = \frac{\text{Fraction Reacted}}{1 - e^{-k_{OH} \times \text{INTOH}}} \quad (V)$$

where k_{OH} is the VOC's rate constant for reaction with OH radicals, and INTOH is a scenario-dependent parameter which reflects the overall integrated radical levels of the scenario. The OH radical rate constants are known for a wide variety of organic compounds (Atkinson 1986, 1989), and methods exist for estimating them for most others (Atkinson 1987).

INTOH values appropriate for a given pollution scenario can be obtained by calculated ratios of amounts reacted to amounts emitted for species with varying OH radical rate constants, and deriving the value where these are fit by equation (V). As discussed by Weir et al (1988), INTOH values for 1-2 day pollution scenarios where ozone levels exceed the Federal ozone standard of 0.12 ppm range from approximately 50 to 170 ppt-min, with a value of approximately 150 ppt-min being chosen to be appropriate for use in maximum reactivity estimates (Weir et al. 1988). Based on this, and the known or estimated OH radical rate constants, kinetic reactivity factors can be readily derived for VOC's which react primarily with OH radicals.

Aldehydes and ketones are also consumed to a non-negligible extent in the atmosphere by photolysis, and alkenes are also consumed by reaction with ozone. Therefore, Equation (V), which is based on assuming that the compound reacts significantly only with OH radicals, will underestimate the kinetic reactivities for these compounds. However, alkenes other than ethene react with OH radicals so rapidly that their kinetic reactivities are calculated to be unity (the maximum value for kinetic reactivity) even if these other processes are ignored, so ethene is the only alkene where consumption by other reactions need to be considered in estimates of kinetic reactivity. To determine how to correct for these additional reactions, ratios of amounts reacted to amounts emitted were calculated for formaldehyde, acetaldehyde, propionaldehyde, acetone, methylethyl ketone, and ethene were calculated for a variety of idealized pollution scenarios (listed below), and the results were compared with mechanistic reactivities calculated using Equation (V). It was found that for those scenarios where the Federal ozone standard of 0.12 ppm was exceeded, the kinetic reactivities could be approximated, to within approximately 10%, by

$$\text{Kinetic Reactivity} = \frac{\text{Correction Factor}}{1 - e^{-k_{OH} \times \text{INTOH}}}, \quad (\text{VI})$$

where INTOH is the same as derived for compounds which react only with OH radicals, and the correction factors are as follows:

Compound	Kinetic Reactivity Correction Factor
-----	-----
Formaldehyde	1.3
Acetaldehyde	1.05
Propionaldehyde	1.03
Acetone	4.6
Methylethyl ketone	1.2
Ethene	1.1

The estimates of maximum kinetic reactivities for individual compounds are given below following the discussion of the estimates of mechanistic reactivities.

ESTIMATES OF MAXIMUM MECHANISTIC REACTIVITIES

Mechanistic reactivities reflect the amount of ozone formed due to the reaction of a given amount of the VOC, independently (to a first approximation at least) of how rapidly the compound reacts. They are determined by the nature of the VOCs reaction mechanism, such the number of conversions of NO to NO₂ which occur during its oxidation process, whether its reactions enhance or inhibit radical or NO_x levels, and the reactivities of the products they form. To provide a basis for estimating maximum mechanistic reactivities for various types of VOCs, these were calculated for a variety of VOCs for the conditions of the representative scenarios discussed above. As discussed by Weir et al (1988), for some VOC's the mechanistic reactivities were calculated directly, while for others they were estimated based on mechanistic reactivities calculated for various "pure mechanism" species representing various aspects of the VOC's reaction mechanism. Examples of mechanistic reactivities calculated for a variety of compounds and scenarios are given elsewhere (Carter and Atkinson 1989, Weir et al. 1988).

In general, for each type of scenario, the mechanistic reactivities for VOCs are highly dependent on the ROG/NO_x ratio, with the maximum mechanistic reactivities being calculated to occur at ROG/NO_x ratios which are somewhat lower than the ratio which is most favorable for ozone formation. The ROG/NO_x ratios for which the highest VOC reactivities were approximately 6 for the EKMA-1 scenarios and 4 (or less) for the EKMA-3 scenarios. The maximum mechanistic reactivities for a given VOC was found to be somewhat less sensitive to the type of scenario, though the type of scenario had some effect on the ROG/NO_x ratio where the maximum reactivities occurred. Generally the mechanistic reactivities tended to be higher for the scenarios employing the Multi-Day formulation, and (except for the higher alkanes) in the scenarios employing the "E" surrogate to represent base case ROG emissions. The nature of the base case ROG surrogate tended to affect the maximum mechanistic reactivities compounds which tend to be radical initiators. For example, for formaldehyde, a radical initiator compound with the highest per-carbon mechanistic reactivities, the calculated maximum mechanistic reactivities range from approximately 3-4 for the scenarios using Surrogate "A" to 5-10 for the scenarios using Surrogate "E". (The values given are moles ozone formed per mole formaldehyde reacted.) Maximum mechanistic reactivities for compounds which did not have significant radical sources in their mechanism were less dependent on the type of scenario. For example, the maximum mechanistic reactivities of propane ranged from a minimum of approximately 0.8 to a maximum of approximately 1.2 moles ozone per mole carbon propane reacted for the various types of scenarios employed.

For most compounds except for several of the higher n-alkanes, the highest mechanistic reactivities were calculated for the conditions of the Multi-Day, Surrogate "E" scenario at the ROG/NO_x ratio of 6. For several of the higher alkanes, slightly higher reactivities were calculated for the Multi-Day, Surrogate "A" scenario at ROG/NO_x = 5. The estimates of maximum mechanistic reactivities used in this study for a given type of VOC is based on the higher of the values calculated for these two scenarios. These values are tabulated in the following section.

RESULTS

MAXIMUM REACTIVITY ESTIMATES FOR SPECIFIC VOC SPECIES

Maximum kinetic and mechanistic reactivity were estimated for all VOC model species for which mechanistic assignments are included in the current detailed SAPRC mechanism. These include all of the compounds identified in the ARB's recent detailed analysis of the composition of evaporative and exhaust emissions from variously-fueled vehicles (ARB 1989), as well as a number of other compounds which were not reported in that analysis. Thus these should be sufficient for the purpose of deriving estimates of ozone impacts from VOC emissions from motor vehicles. These species are listed in Table 1, which indicates the nomenclature used for them in the subsequent tabulations.

For each of these model species, Table 1 gives the T = 300K OH radical rate constants used in the current SAPRC mechanism (Carter 1989b), the estimated kinetic reactivity calculated for INTOH = 150 ppt-min, the calculated or estimated maximum mechanistic reactivities, and the estimated maximum incremental reactivities. Footnotes to the table indicate how the various reactivity factors were derived for the cases where special considerations are involved. The mechanistic and incremental reactivities are given in units of moles of ozone formed per mole carbon VOC reacted, or emitted, respectively. The table also gives the number of carbons and molecular weights for these species, and the corresponding incremental reactivities in terms of grams ozone formed per gram VOC emitted. (These are referred to as the "gram" reactivities as opposed to the "molar" reactivities.) These gram reactivities are the quantities used to estimate maximum ozone impacts of VOC emissions.

ESTIMATION OF MAXIMUM OZONE IMPACTS OF VOC EMISSIONS FROM VARIOUS MOTOR VEHICLES

The application of the maximum reactivity estimates given in Table 1 is illustrated by estimating overall maximum reactivities of emissions from the motor vehicles recently tested by the ARB (ARB 1989). The specific vehicles and fuels for which emissions data were reported are as follows:

1. Two 1987 Ford Crown Victoria Flexible Fuel Vehicles was tested using Indolene Clear fuel. This is taken to represent vehicles using standard gasoline. The resulting emissions are referred to as "Indolene" in the subsequent discussion.
2. The above vehicles were also tested using an 85% methanol, 15% unleaded gasoline combination. The emissions are referred to as "M85".

Table 1. Summary of Maximum Ozone Reactivity Estimates and Related Data for Individual VOC Species Represented in the Detailed SAPRC Mechanism.

Compound or VOC Classification (and footnotes)	Model Species	No. C's	Molec. Wt.	kOH (a)	Kinet. React'y (b)	Mech. React'y (c)	React'y /Mole C (d)	React'y/Gram Carbon (e)	Ozone (f)
Carbon Monoxide	CO	1	28.0	0.35	0.051	1.1	0.057	0.022	0.097
Methane	METHANE	1	16.0	0.01	0.002	6.2	0.012	0.002	0.036
Ethane	ETHANE	2	30.1	0.40	0.059	2.6	0.152	0.047	0.49
Propane	PROPANE	3	44.1	1.79	0.24	1.3	0.307	0.20	1.00
n-Butane	N-C4	4	58.1	3.8	0.43	1.3	0.56	0.36	1.85
n-Pentane	N-C5	5	72.2	5.8	0.58	0.85	0.49	0.48	1.64
n-Hexane	N-C6	6	86.2	7.9	0.69	0.65	0.45	0.58	1.50
n-Heptane	N-C7	7	100.2	9.9	0.77	0.45	0.35	0.65	1.17
n-Octane	N-C8	8	114.2	12.0	0.83	0.35	0.29	0.70	0.98
n-Nonane	N-C9	9	128.3	14.0	0.88	0.30	0.26	0.74	0.89
n-Decane	N-C10	10	142.3	16.1	0.91	0.25	0.23	0.77	0.77
n-Undecane	N-C11	11	156.3	18.2	0.93	0.20	0.19	0.79	0.63
n-Dodecane	N-C12	12	170.3	20.2	0.95	0.20	0.19	0.80	0.64
n-Tridecane	N-C13	13	184.4	22.3	0.96	0.17	0.16	0.81	0.55
n-Tetradecane	N-C14	14	198.4	24.3	0.97	0.15	0.15	0.82	0.49
n-Pentadecane	N-C15	15	212.4	26.4	0.98	0.15	0.15	0.83	0.50
Isobutane	ISO-C4	4	58.1	3.5	0.41	1.8	0.74	0.34	2.43
Lumped C4-C5 Alkanes (g)	C4C5	5	65.1	4.7	0.51	1.1	0.56	0.47	2.06
Branched C5 Alkanes	BR-C5	5	72.2	5.9	0.59	1.1	0.64	0.49	2.14
Iso-Pentane	ISO-C5	5	72.2	5.9	0.59	1.1	0.64	0.49	2.14
Neopentane	NEO-C5	5	72.2	1.11	0.15	1.3	0.20	0.12	0.66
2-Methyl Pentane	2-ME-C5	6	86.2	7.9	0.70	1.0	0.70	0.59	2.32
3-Methylpentane	3-ME-C5	6	86.2	8.5	0.72	1.0	0.72	0.60	2.40
Branched C6 Alkanes	BR-C6	6	86.2	7.9	0.70	1.0	0.70	0.59	2.32
2,3-Dimethyl Butane	23-DMB	6	86.2	8.0	0.70	0.7	0.49	0.59	1.63
2,2-Dimethyl Butane	22-DMB	6	86.2	2.7	0.33	1.1	0.37	0.28	1.23
Lumped C6+ Alkanes (g)	C6PLUS	7	98.2	9.0	0.74	0.7	0.52	0.63	1.78
2,4-Dimethyl Pentane	24-DM-C5	7	100.2	10.0	0.78	1.0	0.78	0.65	2.61
3-Methyl Hexane	3-ME-C6	7	100.2	10.5	0.79	0.75	0.60	0.66	2.00
4-Methyl Hexane	4-ME-C6	7	100.2	10.5	0.79	0.75	0.60	0.66	2.00
Branched C7 Alkanes	BR-C7	7	100.2	10.5	0.79	0.75	0.60	0.66	2.00
2,3-Dimethyl Pentane	23-DM-C5	7	100.2	10.6	0.80	0.80	0.64	0.67	2.13
Iso-Octane	ISO-C8	8	114.2	6.9	0.64	0.85	0.55	0.54	1.84
4-Methyl Heptane	4-ME-C7	8	114.2	12.6	0.85	0.60	0.51	0.72	1.71
Branched C8 Alkanes	BR-C8	8	114.2	12.6	0.85	0.60	0.51	0.72	1.71
Branched C9 Alkanes	BR-C9	9	128.3	15.4	0.90	0.50	0.45	0.76	1.52
4-Ethyl Heptane	4-ET-C7	9	128.3	15.4	0.90	0.50	0.45	0.76	1.52
Branched C10 Alkanes	BR-C10	10	142.3	17.5	0.93	0.45	0.42	0.78	1.41
34-Propyl Heptane	4-PR-C7	10	142.3	17.5	0.93	0.45	0.42	0.78	1.41
Branched C11 alkanes	BR-C11	11	156.3	21.0	0.96	0.45	0.43	0.81	1.45
Branched C12 Alkanes	BR-C12	12	170.3	23.0	0.97	0.45	0.44	0.82	1.47
Branched C13 Alkanes	BR-C13	13	184.4	25.1	0.98	0.40	0.39	0.83	1.32
Branched C14 Alkanes	BR-C14	14	198.4	27.1	0.98	0.30	0.29	0.83	1.00
Branched C15 Alkanes	BR-C15	15	212.4	29.2	0.99	0.30	0.30	0.84	1.00

(continued)

Table 1 (continued)

Compound or VOC Classification (and footnotes)	Model Species	No. C's	Molec. Wt.	kOH (a)	Kinet. React'y (b)	Mech. React'y (c)	React'y /Mole C (d)	-React'y/ Carbon (e)	Gram- Ozone (f)
Cyclopentane	CYCC5	5	70.1	8.2	0.71	1.6	1.14	0.61	3.89
Methylcyclopentane	ME-CYCC5	6	84.2	10.4	0.79	1.4	1.11	0.68	3.79
C6 Cycloalkanes	CYC-C6	6	84.2	12.3	0.84	0.65	0.55	0.72	1.88
Cyclohexane	CYCC6	6	84.2	12.3	0.84	0.65	0.55	0.72	1.88
C7 Cycloalkanes	CYC-C7	7	98.2	15.0	0.89	0.80	0.72	0.76	2.45
Methylcyclohexane	ME-CYCC6	7	98.2	15.0	0.89	0.80	0.72	0.76	2.45
Ethylcyclohexane	ET-CYCC6	8	112.2	17.9	0.93	0.85	0.79	0.80	2.71
C8 Cycloalkanes	CYC-C8	8	112.2	17.9	0.93	0.85	0.79	0.80	2.71
C9 Cycloalkanes	CYC-C9	9	126.2	20.5	0.95	0.90	0.86	0.81	2.94
C10 Cycloalkanes	CYC-C10	10	140.3	23.4	0.97	0.75	0.73	0.83	2.49
C11 Cycloalkanes	CYC-C11	11	154.3	26.0	0.98	0.70	0.69	0.84	2.35
C12 Cycloalkanes	CYC-C12	12	168.3	28.9	0.99	0.65	0.64	0.85	2.20
C13 Cycloalkanes	CYC-C13	13	182.4	31.0	0.99	0.50	0.50	0.85	1.69
C14 Cycloalkanes	CYC-C14	14	196.4	33.0	0.99	0.50	0.50	0.85	1.70
C15 Cycloalkanes	CYC-C15	15	210.4	35.1	0.99	0.45	0.45	0.85	1.53
Ethene (h)	ETHENE	2	28.0	12.4	0.93	4.8	4.46	0.80	15.25
Propene (i)	PROPENE	3	42.1	38.2	1.00	3.7	3.70	0.86	12.66
C4 Terminal Alkanes	C4-OLE1	4	56.1	45.6	1.00	3.5	3.50	0.86	11.98
1-Butene	1-BUTENE	4	56.1	45.6	1.00	3.5	3.50	0.86	11.98
2-Methyl-1-Butene	2M-1-BUT	5	70.1	88.0	1.00	2.4	2.40	0.86	8.21
3-Methyl-1-Butene	3M-1-BUT	5	70.1	46.1	1.00	2.4	2.40	0.86	8.21
1-Pentene	1-PENTENE	5	70.1	45.6	1.00	2.4	2.40	0.86	8.21
C5 Terminal Alkanes	C5-OLE1	5	70.1	45.6	1.00	2.4	2.40	0.86	8.21
1-Hexene	1-HEXENE	6	84.2	53.7	1.00	1.6	1.60	0.86	5.48
C6 Terminal Alkanes	C6-OLE1	6	84.2	53.7	1.00	1.6	1.60	0.86	5.48
C7 Terminal Alkanes	C7-OLE1	7	98.2	53.7	1.00	1.3	1.30	0.86	4.45
C8 Terminal Alkanes	C8-OLE1	8	112.2	53.7	1.00	1.0	1.00	0.86	3.42
C9 Terminal Alkanes	C9-OLE1	9	126.2	53.7	1.00	0.8	0.80	0.86	2.74
C10 Terminal Alkanes	C10-OLE1	10	140.3	53.7	1.00	0.7	0.70	0.86	2.40
C11 Terminal Alkanes	C11-OLE1	11	154.3	53.7	1.00	0.6	0.60	0.86	2.05
C12 Terminal Alkanes	C12-OLE1	12	168.3	53.7	1.00	0.5	0.50	0.86	1.71
C13 Terminal Alkanes	C13-OLE1	13	182.4	53.7	1.00	0.45	0.45	0.86	1.54
C14 Terminal Alkanes	C14-OLE1	14	196.4	53.7	1.00	0.40	0.40	0.86	1.37
C15 Terminal Alkenes	C15-OLE1	15	210.4	53.7	1.00	0.40	0.40	0.86	1.37
Isobutene	ISOBUTEN	4	56.1	74.6	1.00	2.1	2.10	0.86	7.19
cis-2-Butene	C-2-BUTE	4	56.1	81.9	1.00	3.9	3.90	0.86	13.35
trans-2-Butene	T-2-BUTE	4	56.1	92.4	1.00	3.9	3.90	0.86	13.35
C4 Terminal Alkenes	C4-OLE2	4	56.1	92.4	1.00	3.9	3.90	0.86	13.35
2-Methyl-2-Butene	2M-2-BUT	5	70.1	126.3	1.00	3.3	3.30	0.86	11.29
C5 Terminal Alkenes	C5-OLE2	5	70.1	92.4	1.00	3.3	3.30	0.86	11.29
2,3-Dimethyl-2-Butene	23M2-BUT	6	84.2	159.5	1.00	2.8	2.80	0.86	9.58
C6 Terminal Alkenes	C6-OLE2	6	84.2	92.4	1.00	2.8	2.80	0.86	9.58
C7 Terminal Alkenes	C7-OLE2	7	98.2	92.4	1.00	2.3	2.30	0.86	7.87
C8 Terminal Alkenes	C8-OLE2	8	112.2	92.4	1.00	1.9	1.90	0.86	6.50
C9 Terminal Alkenes	C9-OLE2	9	126.2	92.4	1.00	1.6	1.60	0.86	5.48

(continued)

Table 1 (continued)

Compound or VOC Classification (and footnotes)	Model Species	No. C's	Molec. Wt.	kOH (a)	Kinet. React'y (b)	Mech. React'y (c)	React'y /Mole C (d)	-React'y/Gram- Carbon (e)	Gram- Ozone (f)
C10 Terminal Alkenes	C10-OLE2	10	140.3	92.4	1.00	1.4	1.40	0.86	4.79
C11 Terminal Alkenes	C11-OLE2	11	154.3	92.4	1.00	1.3	1.30	0.86	4.45
C12 Terminal Alkenes	C12-OLE2	12	168.3	92.4	1.00	1.2	1.20	0.86	4.11
C13 Terminal Alkenes	C13-OLE2	13	182.4	92.4	1.00	1.1	1.10	0.86	3.76
C14 Terminal Alkenes	C14-OLE2	14	196.4	92.4	1.00	1.0	1.00	0.86	3.42
C15 Terminal Alkenes	C15-OLE2	15	210.4	92.4	1.00	0.9	0.90	0.86	3.08
1,3-Butadiene	13-BUTDE	4	54.1	96.7	1.00	4.1	4.10	0.89	14.55
Isoprene	ISOPRENE	5	68.1	146.3	1.00	3.5	3.50	0.88	12.33
Cyclopentene	CYC-PNTE	5	68.1	97.4	1.00	2.2	2.20	0.88	7.75
Cyclohexene	CYC-HEXE	6	82.2	98.2	1.00	1.8	1.80	0.88	6.31
b-Pinene (j)	B-PINENE	10	136.2	114.8	1.00	1.0	1.00	0.88	3.52
a-Pinene	A-PINENE	10	136.2	78.0	1.00	1.0	1.00	0.88	3.52
C4 Alkenes (k)	C4-OLE	4	56.1	69.0	1.00	3.7	3.70	0.86	12.66
C5 Alkenes (k)	C5-OLE	5	70.1	69.0	1.00	2.9	2.90	0.86	9.92
C6 Alkenes (k)	C6-OLE	6	84.2	73.1	1.00	2.2	2.20	0.86	7.53
C7 Alkenes (k)	C7-OLE	7	98.2	73.1	1.00	1.8	1.80	0.86	6.16
C8 Alkenes (k)	C8-OLE	8	112.2	73.1	1.00	1.8	1.80	0.86	6.16
C9 Alkenes (k)	C9-OLE	9	126.2	73.1	1.00	1.8	1.80	0.86	6.16
C10 Alkenes (k)	C10-OLE	10	140.3	73.1	1.00	1.1	1.10	0.86	3.76
C11 Alkenes (k)	C11-OLE	11	154.3	73.1	1.00	1.0	1.00	0.86	3.42
C12 Alkenes (k)	C12-OLE	12	168.3	73.1	1.00	0.8	0.80	0.86	2.74
C13 Alkenes (k)	C13-OLE	13	182.4	73.1	1.00	0.8	0.80	0.86	2.74
C14 Alkenes (k)	C14-OLE	14	196.4	73.1	1.00	0.7	0.70	0.86	2.40
C15 Alkenes (k)	C15-OLE	15	210.4	73.1	1.00	0.7	0.70	0.86	2.40
Benzene	BENZENE	6	78.1	1.89	0.25	1.1	0.27	0.23	1.00
Toluene	TOLUENE	7	92.1	8.7	0.73	2.0	1.46	0.67	5.31
Ethyl Benzene	C2-BENZ	8	106.2	10.4	0.79	1.8	1.42	0.71	5.15
Monoalkyl Benzenes	ALK1BENZ	8	106.2	8.7	0.73	1.8	1.31	0.66	4.74
n-Propyl Benzene (l)	N-C3-BEN	9	120.2	8.8	0.73	1.6	1.17	0.66	4.22
Isopropyl Benzene	I-C3-BEN	9	120.2	9.5	0.76	1.6	1.22	0.68	4.38
s-Butyl Benzene (m)	S-C4-BEN	10	134.2	8.8	0.73	1.4	1.03	0.65	3.67
o-Xylene	O-XYLENE	8	106.2	20.1	0.95	3.1	2.95	0.86	10.66
p-Xylene	P-XYLENE	8	106.2	21.0	0.96	3.1	2.97	0.87	10.73
m-Xylene (n)	M-XYLENE	8	106.2	34.6	0.99	3.3	3.28	0.90	11.87
Dialkyl Benzenes (o)	ALK2BENZ	9	120.2	34.6	0.99	2.9	2.88	0.89	10.36
1,3,5-Trimethyl Benzene	135-TMB	9	120.2	84.4	1.00	3.7	3.70	0.90	13.30
1,2,3-Trimethyl Benzene	123-TMB	9	120.2	48.0	1.00	3.2	3.20	0.90	11.49
1,2,4-Trimethyl Benzene	124-TMB	9	120.2	47.7	1.00	3.2	3.20	0.90	11.49
Trialkyl Benzenes (p)	ALK3BENZ	9	120.2	84.4	1.00	3.2	3.20	0.90	11.50
Tetralin and/or Indanes	TETRALIN	10	132.2	50.3	1.00	0.3	0.30	0.91	1.09
Naphthalene	NAPHTHAL	10	128.2	31.7	0.99	0.4	0.40	0.93	1.49
Methyl Naphthalenes	ME-NAPH	11	142.2	76.3	1.00	1.0	1.00	0.93	3.71
Dimethyl Naphthalenes	DM-NAPH	12	156.2	113.0	1.00	1.9	1.90	0.92	7.01

(continued)

Table 1 (continued)

Compound or VOC Classification (and footnotes)	Model Species	No. C's	Molec. Wt.	kOH (a)	Kinet. React'y (b)	Mech. React'y (c)	React'y /Mole C (d)	-React'y/Gram- Carbon (e)	Gram- Ozone (f)
Acetylene	ACETYLEN	2	26.0	1.15	0.16	1.8	0.29	0.15	1.05
Methyl Acetylene	ME-ACTYL	3	40.1	8.9	0.74	2.5	1.84	0.66	6.62
Methanol	MEOH	1	32.0	1.38	0.19	5.0	0.94	0.071	1.40
Ethanol	ETOH	2	46.1	4.8	0.51	2.1	1.08	0.27	2.25
n-Propyl Alcohol	N-C3-OH	3	60.1	7.8	0.69	2.3	1.59	0.41	3.81
Isopropyl Alcohol	I-C3-OH	3	60.1	7.6	0.68	0.5	0.34	0.41	0.82
Isobutyl Alcohol	I-C4-OH	4	74.1	14.0	0.88	0.7	0.61	0.57	1.59
n-Butyl Alcohol	N-C4-OH	4	74.1	12.2	0.84	1.9	1.59	0.54	4.13
t-Butyl Alcohol	T-C4-OH	4	74.1	1.66	0.22	1.6	0.35	0.14	0.91
Dimethyl Ether	ME-O-ME	2	46.1	4.4	0.48	3.6	1.74	0.25	3.64
Ethylene Glycol	ET-GLYCL	2	62.1	11.3	0.82	2.1	1.71	0.32	2.65
Propylene Glycol	PR-GLYCL	3	76.1	17.6	0.93	1.2	1.11	0.44	2.11
Formaldehyde (q)	FORMALD	1	30.0	14.4	1.00	10.3	10.30	0.40	16.46
Acetaldehyde (q)	ACETALD	2	44.0	23.0	1.00	5.3	5.30	0.55	11.55
Propionaldehyde (q)	PROPALD	3	58.1	28.9	1.00	5.0	5.00	0.62	12.40
Acrolein (q,r)	ACROLEIN	3	56.1		1.00	5.0	5.00	0.64	12.84
Acetone (s)	ACETONE	3	58.1	0.34	0.23	2.9	0.67	0.14	1.65
Methyl Ethyl Ketone (t)	MEK	4	72.1	1.70	0.28	4.2	1.16	0.19	3.08
Benzaldehyde (q)	BENZALD	7	106.1	18.9	1.00	0.0	0.00	0.79	0.00
Phenol (u)	PHENOL	6	94.1	38.6	1.00	0.3	0.30	0.77	0.92
Cresols (u)	CRESOL	7	108.1	61.6	1.00	0.7	0.70	0.78	2.17
Unreactive Carbon	INERT	1	14.0	0.0	0.00	0.0	0.00	0.00	0.00

- a. OH radical rate constant in units of $1.0E+3$ ppm⁻¹ min⁻¹, as used in current SAPRC mechanism (Carter 1989b).
- b. Kinetic reactivity is ratio of moles reacted to moles emitted, estimated using INTOH = 150 ppt-min. See footnotes for corrections for compounds where OH reaction is not the only significant loss process.
- c. Molar mechanistic reactivity is estimated maximum moles ozone formed per mole carbon reacted, based on larger of the values calculated for the Multi-Day, Surrogate "E" scenario for ROG/NOx = 6, or the Multi-Day, Surrogate "A" scenario for ROG/NOx = 5.
- d. Overall reactivity is the estimated maximum moles ozone formed per mole carbon emitted, derived by multiplying the estimated maximum kinetic reactivity times the estimated maximum molar mechanistic reactivity.
- e. Estimated grams carbon reacted per gram VOC emitted. Calculated from (Kinetic Reactivity) x (Atomic Weight of Carbon) x (No. Carbons in VOC) / (Molecular Weight of VOC).
- f. Incremental ozone reactivity expressed as estimated maximum grams of ozone formed per gram model species emitted. Calculated from: (Mass Reactivity) = (Molar Reactivity of VOC) x (Molecular Weight of Ozone) x (No. Carbons in VOC) / (Molec. Weight of VOC).

(continued)

Table 1 (concluded)

- g. Lumped species used in the Lurmann et al (1987) mechanism.
- h. Kinetic reactivity of ethene corrected by a factor of 1.1 to correct for estimated amount of additional consumption due to ozone reaction.
- i. Propene and higher alkenes assumed to be completely reacted (kinetic reactivities = 1.0) because of their high OH radical rate constants, and the fact that they also are consumed by ozone reactions.
- j. Mechanistic reactivity of alpha-pinene used.
- k. Current emissions profiles include categories such as "Isomers of Butene" or "C7 Olefins", which do not indicate whether the alkene isomer(s) are have internal or terminal double bonds. In these cases, the reactivity parameters are derived based on assuming they consist of equal amounts of internal and terminal alkenes. The appropriateness of this assumption is unknown.
- l. The reactivity of n-propylbenzene is used for the emissions category designated "propylbenzene".
- m. The reactivity of n-butylbenzene is used for the emissions category designated "Isomers of Butylbenzene".
- o. The model species "ALK2BENZ" is used for the emissions category designated "Isomers of Ethyltoluene".
- p. The model species "ALK3BENZ" is used for the emissions category designated "Trimethylbenzene".
- q. These compounds react by photolysis as well as with OH radicals. Estimated to be essentially completely reacted in scenarios with INTOH = 150 ppt-min.
- r. Assumed to have the same mechanistic reactivity as propionaldehyde.
- s. Kinetic reactivity of acetone corrected by a factor of 4.64 to account for additional consumption due to photolysis.
- t. Kinetic reactivity of methyl ethyl ketone corrected by a factor of 1.22 to account for additional consumption due to photolysis.
- u. These compounds react rapidly with NO₃ radicals as well as with OH radicals. Assumed to be completely reacted in scenarios where ozone (and thus NO₃ radicals) is formed.

3. The above vehicles were also tested using 100% methanol fuel. This is designated "M100". Note that the authors of the ARB report (ARB 1989) did not consider this to be representative of future M100 vehicles.
4. The above vehicles were also tested using two ethanol fuel blends, designated "E95" and "E85".
5. An 1988 dual-fueled LPG/Gasoline Chevrolet 1500 Pickup was used to obtain LPG exhaust data. Evaporative emissions were not reported and are assumed to be negligible.
6. An 1986 dual-fueled CNG/gasoline Buick Park Avenue was used to obtain CNG exhaust data. Evaporative emissions were not reported and are assumed to be negligible.

(Results of tests from electric and hydrogen vehicles were also reported, but are not discussed here.) The results of these tests give grams of CO, methane, and individual NMHCs in the exhaust and (where applicable) evaporative emissions per mile traveled. These data are listed in Appendix D in the ARB (1989) report, and were provided to the author in computer-readable form by the ARB modeling staff.

The estimates of total maximum ozone formed per mile traveled for vehicles using the six types of fuels derived from the tests reported by the ARB are summarized on Table 2, and the breakdown of the contributions of individual chemical groups to the NMHC exhaust and evaporative emissions from these tests are given in the tables the Appendix. The total per-mile ozone reactivities of the exhaust or evaporative emissions are calculated by

$$\begin{aligned}
 \frac{\text{g O}_3}{\text{Mile Travel}} &= \left(\frac{\text{g CO}}{\text{Mile Travel}} \times \frac{\text{g O}_3}{\text{g CO}} \right) + \left(\frac{\text{g CH}_4}{\text{Mile Travel}} \times \frac{\text{g O}_3}{\text{g CH}_4} \right) \\
 &+ \left(\frac{\text{g NMHC}}{\text{Mile Travel}} \times \frac{\text{g O}_3}{\text{g NMHC}} \right) \quad \text{(VII)}
 \end{aligned}$$

where (from Table 1)

$$\begin{aligned}
 \frac{\text{g O}_3}{\text{g CO}} &= 0.097, & \frac{\text{g O}_3}{\text{g CH}_4} &= 0.036, \\
 \text{Emit.} & & \text{Emit.} &
 \end{aligned}$$

and

$$\frac{\text{g O}_3}{\text{g NMHC}} = \text{SUM}_i \left(\frac{\text{g VOC}(i)}{\text{g NMHC}} \times \frac{\text{g O}_3}{\text{g VOC}(i)} \right), \quad \text{(VIII)}$$

and VOC(i) refers to the i'th individual non-methane organic compound in the exhaust or evaporative emissions, and "g O3/g VOC(i) emitted" is the

Table 2. Estimated Maximum Ozone Reactivities [a] and Carbon Reacted [b] for Emissions from Vehicles Using Various Fuels, Derived from the Tests Reported by ARB (1989).

Fuel	Emissions Source	Grams /Mile	Carbon Reacted		Ozone Reactivity	
			/Gram	/Mile	/Gram	/Mile
Indolene	Exh. CO	1.35	0.02	0.03	0.10	0.13
	Exh. CH4	0.08	0.002	0.00	0.04	0.00
	Exh. NMHC	0.35	0.60	0.21	4.35	1.51
	Evap. NMHC	0.05	0.63	0.03	3.45	0.16
	Total	1.82		0.27		1.80
E95	Exh. CO	1.93	0.02	0.04	0.10	0.19
	Exh. CH4	0.19	0.002	0.00	0.04	0.01
	Exh. NMHC	0.94	0.33	0.31	3.59	3.38
	Evap. NMHC	0.03	0.36	0.01	2.51	0.08
	Total	3.10		0.36		3.66
E85	Exh. CO	1.85	0.02	0.04	0.10	0.18
	Exh. CH4	0.17	0.002	0.00	0.04	0.01
	Exh. NMHC	1.02	0.34	0.35	3.46	3.53
	Evap. NMHC	0.05	0.34	0.02	2.55	0.13
	Total	3.08		0.41		3.85
M85	Exh. CO	1.01	0.02	0.02	0.10	0.10
	Exh. CH4	0.04	0.002	0.00	0.04	0.00
	Exh. NMHC	0.25	0.26	0.06	3.50	0.86
	Evap. NMHC	0.09	0.26	0.02	2.00	0.18
	Total	1.39		0.10		1.14
M100	Exh. CO	1.47	0.02	0.03	0.10	0.14
	Exh. CH4	0.02	0.002	0.00	0.04	0.00
	Exh. NMHC	0.56	0.11	0.06	2.44	1.36
	Evap. NMHC	0.15	0.12	0.02	1.66	0.24
	Total	2.19		0.11		1.74
LPG	Exh. CO	1.40	0.02	0.03	0.10	0.14
	Exh. CH4	0.05	0.002	0.00	0.04	0.00
	Exh. NMHC	0.20	0.31	0.06	3.54	0.71
	Total	1.65		0.09		0.85
CNG	Exh. CO	0.07	0.02	0.00	0.10	0.01
	Exh. CH4	1.80	0.002	0.00	0.04	0.06
	Exh. NMHC	0.19	0.17	0.03	1.90	0.36
	Total	2.06		0.03		0.43

a. Grams ozone formed per gram VOC emitted or grams ozone formed per mile traveled.

b. Grams carbon atoms undergoing chemical reaction per gram VOC emitted, or grams carbon reacting per mile traveled.

gram reactivity of VOC(i) listed in Table 1. [Equations (VII) and (VIII) are based on the principle that incremental reactivities of mixtures are linear sums of the incremental reactivities of their components. This follows mathematically because, as discussed by Carter and Atkinson (1989), incremental reactivities are defined as the limit as the amount of test VOC in Equation (I) approaches zero.] The reactivity contributions from CO and methane are separated from those of the NMHCs because these are generally measured and reported separately in emissions tests of motor vehicles. However, it can be seen that CO and (for CNG vehicles) methane have non-negligible contributions to ozone formation from vehicle emissions, and their contributions to reactivity need to be taken into account along with those of the other components of vehicle emissions.

Table 3 gives a summary of the reactivity rankings of the emissions from the vehicles using the various alternative fuels with those from the vehicles using the Indolene fuel. These comparisons are given both in terms of estimates of maximum ozone formation potential per mile traveled, and in terms of reactivities per gram of exhaust and evaporative NMHC emissions. The table also compares the relative amounts of NMHC emitted per mile for the various tests, and relative amounts of carbon in the emitted VOCs which are estimated to undergo chemical reaction (calculated from the kinetic reactivities as indicated in Footnote (e) to Table 1. In addition, the table also gives the relative reactivities for the exhaust NMHC emissions given in the ARB (1989) report, derived based on assuming that reactivity is proportional to the OH radical rate constant (see Discussion).

The maximum ozone reactivity estimates given on Tables 1-3 do not necessarily reflect the VOC reactivities for any specific pollution scenario, but reflect results of estimates of maximum fractions of emitted VOCs which undergo chemical reaction in the atmosphere, combined with separate estimates of maximum amounts of ozone formed when a given amount of VOC reacts. Reactivities for specific scenarios would in general be lower, either because lower fractions of VOCs react (i.e., because of lower kinetic reactivities) or because less ozone is formed per reacting VOC (lower mechanistic reactivities), or both. To illustrate this, Table 4 compares the maximum ozone reactivity estimates with reactivities directly calculated for several specific scenarios for the various exhaust NMHC mixtures in the ARB (1989) report. The reactivities calculated for the Multi-Day scenarios with Surrogate "E" and ROG/NOx=6 and with Surrogate "A" and ROG/NOx=5 are shown because these are the scenarios which were used to derive the maximum mechanistic reactivity estimates. In these cases, the reactivities are somewhat lower than the estimated maximum values because the kinetic reactivities in these scenarios are less than assumed when making the maximum reactivity estimates. (The values of the INTOH parameter, which determines the kinetic reactivity given the OH radical rate constant [Equation (V) or (VI)], are respectively 63.3 and 82.1 ppt-min for these two scenarios, compared to the value of 150 ppt-min used in the maximum reactivity estimates [see above].) On the other hand, the kinetic reactivities in the EKMA-1, Surrogate "A" scenario at ROG/NOx=10, the ratio most favorable for ozone formation, are relatively high (since INTOH = 160 ppt-min for that

Table 3. Rankings of Reactivities of Emissions from Vehicles Using Various Alternative Fuels, Relative to Those from Gasoline (Indolene) Vehicles, Derived from the Results of the ARB (1989) Analysis.

Reactivity Measure	--- Reactivity Relative to Indolene ---					
	E95	E85	M85	M100	LPG	CNG

Total Reactivity/Mile						
Maximum Ozone	2.03	2.14	0.63	0.97	0.47	0.24
Total Carbon Reacted	1.33	1.52	0.37	0.41	0.33	0.26
Grams NMHC Emitted	2.49	2.73	0.86	1.79	0.51	0.48
Exhaust NMHC Reactivity/Gram						
Maximum Ozone	0.83	0.80	0.81	0.56	0.81	0.44
Carbon Reacted	0.56	0.57	0.43	0.18	0.52	0.29
Linear kOH (ARB 1989)	(a)	(a)	0.65	(a)	0.89	0.48
Evap. NMHC Reactivity/Gram						
Maximum Ozone	0.73	0.74	0.58	0.48	-	-
Carbon Reacted	0.56	0.54	0.42	0.18	-	-
Linear kOH (ARB 1989)	(a)	(a)	0.67	(a)	-	-

a. Not reported.

Table 4. Comparisons of Estimates of Maximum Ozone Reactivities with Ozone Reactivities Calculated for Selected Scenarios for Exhaust NMHC Emissions from Various Fuel Vehicles (ARB 1989).

Reactivity Derivation (a)	-- NMHC Exhaust Reactivity (g ozone/g NMHC) --						
	INDO	E95	E85	M85	M100	LPG	CNG
Maximum Reactivity	4.35	3.59	3.46	3.50	2.44	3.54	1.90
MD, Surg-E, C/N=6	3.08	2.14	2.12	2.45	1.50	2.38	1.33
MD, Surg-A, C/N=5	2.43	1.89	1.85	1.59	0.93	1.78	1.01
EK-1, Surg-A, C/N=6	1.83	1.30	1.29	1.24	0.75	1.38	0.77
EK-1, Surg-A, C/N=10	0.48	0.44	0.43	0.36	0.25	0.50	0.26
EK-1, Surg-A, C/N=16	0.21	0.22	0.20	0.18	0.13	0.29	0.14
	----- Reactivity Relative to Indolene -----						
Maximum Reactivity	1.0	0.83	0.80	0.81	0.56	0.81	0.44
MD, Surg-E, C/N=6	1.0	0.69	0.69	0.80	0.49	0.77	0.43
MD, Surg-A, C/N=5	1.0	0.78	0.76	0.65	0.38	0.73	0.42
EK-1, Surg-A, C/N=6	1.0	0.71	0.70	0.68	0.41	0.75	0.42
EK-1, Surg-A, C/N=10	1.0	0.91	0.88	0.74	0.51	1.04	0.54
EK-1, Surg-A, C/N=16	1.0	1.03	0.93	0.84	0.64	1.36	0.67

- a. Designations used: "Maximum Reactivity": estimated based on separate estimates of maximum kinetic and mechanistic reactivities for the individual VOC exhaust constituents as described in the text. "MD": Multi-Day scenario; "Surg-A": Scenario employed base case ROG surrogate based on air quality data; "Surg-E": Scenario employed base case ROG surrogate based on emissions data; "C/N": Base case ROG/NOx ratio employed in the scenario.

scenario), but the mechanistic reactivities are much lower, resulting in lower overall reactivities. The differences in reactivities for the EKMA-1, Surrogate "A" scenarios at the various ROG/NOx ratios are due primarily to effects of ROG/NOx ratios on mechanistic reactivities.

DISCUSSION

The maximum ozone reactivity estimates discussed in this report can provide a basis for deriving a ranking scale for motor vehicle emissions which is based directly on estimates of maximum potentials for ozone formation. Given the results of vehicle emissions tests such as those given in the ARB (1989) report, and ozone reactivity factors for individual VOCs such as those in Table 1, vehicle emissions can be rated on the basis of estimates ozone formation per mile traveled. Since it takes differences of chemical reactivities into account, such a scale has obvious utility in assessing relative ozone benefits of use of various alternative fuels, and in assessing relative advantages of strategies involving reducing fuel and exhaust reactivity as opposed to strategies involving reduction of total VOC emissions of conventionally fueled vehicles.

Clearly, if one wishes to carry out the most accurate possible assessment of effects of ozone formation of a specific strategy involving emissions changes under a specific set of airshed conditions, detailed grid model calculations of the type carried out in the Carnegie-Mellon study (Russell et al. 1989) are required. However, this requires highly expensive calculations on powerful computers using models with extremely large data input requirements. This is not practical for routine assessment purposes. On the other hand, the proposed method for reactivity assessment of vehicle emissions can be readily carried out on a personal computer using a simple "spreadsheet" type program, requiring as input only the reactivity factors for the individual VOCs (as given in the last column in Table 1), and the results of the speciated analysis of the vehicle emissions. Given a suitably comprehensive vehicle testing program, this method allows for screening of ozone impacts from a wide variety of different types of vehicles, and indicate which vehicle or fuel modification approaches might be worthy of a more extensive analysis using more detailed models.

It should be recognized, however, that the development of a single reactivity scale for assessing ozone impacts of VOC emissions has a number of significant uncertainties, both of a scientific and technical and of a policy nature. The scientific and technical uncertainties include the following:

- (1) The appropriateness of the pollution scenarios used in this study to derive the maximum kinetic and mechanistic reactivity estimates has not been established. These scenarios are highly idealized and are not intended to represent the conditions of any specific airshed. Instead

they are designed to represent the range of chemical conditions which might affect reactivity. The author believes that they are probably appropriate for this purpose, but they have not been independently evaluated by other experts in the air pollution modeling field. Such an independent peer review should be carried out before these scenarios are used as a basis for policy decisions. In addition, reactivity predictions using these idealized scenarios should be tested against reactivity predictions using realistic grid-type urban airshed models, such as the System Applications AIRSHED model, the Caltech/ Carnegie-Mellon airshed model, or the ARB's recently-developed CALGRID model.

(2) The composition of the base case ROG emissions used in the pollution scenarios is also uncertain. As discussed elsewhere (Weir et al. 1989), mechanistic reactivities calculated using a base case ROG surrogate mixture based on emissions data can in some cases differ by as much as a factor of two from those calculated using a surrogate derived based on air quality data. The mechanistic reactivities of formaldehyde and (to a lesser extent) other species which have significant radical sources or sinks in their mechanisms are particularly sensitive to this. The main difference between these two base case ROG surrogates is that the surrogate derived from air quality data has significantly higher aldehydes than indicated by the emissions data. The emissions inventories may well be deficient in aldehyde sources, suggesting that the air quality-derived surrogate may be more appropriate. However, the ambient aldehyde data used to derive of the relatively high aldehyde levels in the air quality-derived surrogate are limited and highly scattered (see for example Figure 4-2 in Lurmann et al [1987]), and aldehyde assumed in the "A" surrogate are based on the maximum levels observed. Note that the mechanistic reactivities derived for formaldehyde and other radical source species are based on those calculated for scenarios using the emissions-based surrogate, since these give the highest estimated reactivities.

(3) There continue to be significant uncertainties in our knowledge of the atmospheric chemistry of organic compounds, resulting in corresponding uncertainties in the calculated mechanistic reactivities for many of the VOCs. Although the mechanism used in this study has been extensively tested against the available environmental chamber data (see Carter 1989b and references therein), suitable environmental chamber data are available for testing the mechanisms of only a relatively limited number of VOCs, and the mechanisms for most other compounds are based on estimations and extrapolations. The reactivities for the higher molecular weight species are particularly uncertain. A discussion of these mechanistic uncertainties is beyond the scope of this report, but it should be recognized that in some cases they can be significant.

Despite the significant scientific and technical uncertainties, perhaps the most difficult problem in deriving an ozone reactivity for VOCs is more of a policy rather than a technical nature. This problem arises from the fact that amounts of ozone formation caused by emissions of VOCs depend significantly on the conditions under which the VOC is emitted, while in practice most policy makers and regulators are unwilling to take

reactivity considerations into account unless a single reactivity scale can be derived which applicable under all relevant conditions. In this work, the use of the "maximum reactivity" criterion is proposed as a means to deal with this problem. As indicated above, this scale is based on estimates of maximum amounts of ozone formation the VOC could reasonably be expected to cause when emitted into the atmosphere. This approach not only provides a means to derive a single scale despite the dependence of reactivities on conditions, but also provides a means to deal with technical uncertainties in the model formulation and the chemical mechanism (Weir et al. 1989).

However, the "maximum reactivity" criterion is subject to the obvious criticism that it does not necessarily represent the conditions of any specific airshed. In addition, the conditions where VOCs have the highest reactivity are not the same as the conditions most favorable for total ozone formation, since generally the maximum VOC reactivities occur at ROG/NOx ratios below the "optimum" value for ozone. On the other hand, the maximum reactivity scale by definition reflects those conditions where VOC control has the greatest effect on ozone formation. As shown on Table 4, above, reactivities rankings for conditions of specific pollution scenarios can in some cases be quite different from maximum reactivity rankings, even if they are considered in a relative rather than an absolute sense. However, the data on Table 4 also shows that a reactivity scale derived to represent the conditions of one airshed may be totally inappropriate for another, particularly if the two airsheds have significantly different NOx levels. Therefore, those who criticize the maximum method for deriving a single reactivity should either propose an alternative which is more justifiable, or attempt to convince policy makers and regulators to use different reactivity scales for different airsheds.

An alternative method for deriving a reactivity scale which has been proposed, and which was used by the ARB staff in its recent analysis of vehicle emissions (ARB 1989), is to assume that VOC reactivity is proportional to its OH radical rate constant. (This is designated as the "linear kOH" scale on Table 3 and in the subsequent discussion.) This has the significant advantage of simplicity and ease of derivation -- it is independent of the environment in which the VOC is emitted, and that the OH radical rate constant for most VOCs emitted into the atmosphere are either known or can be estimated (Atkinson, 1986, 1987, 1989). The scientific basis for this scale is the fact that most (though not all) VOCs are consumed in the atmosphere by reaction with OH radicals, and that the rate of this reaction thus controls the rate at which the VOC causes ozone formation. This method clearly does not take differences of reaction mechanisms into account, a fact which is well recognized by most who use it (e.g. see ARB 1989). Another problem with the linear kOH scale which is apparently not as generally recognized is the fact that the impact of emissions of a VOC on air quality is less a function of how rapidly the VOC reacts than of how much of the VOC reacts. For VOCs which react relatively slowly, the amount of VOC which reacts is proportional to the rate at which it reacts, and the linear kOH method will give appropriate rankings of how much of the VOCs react in a

pollution scenario, and thus (to a first approximation) their relative reactivity. However, for VOCs which react so rapidly that all the emitted VOC is consumed in the scenario, and thus the amount of the VOC which reacts, will be independent of its rate of reaction. For VOCs with intermediate rates of reaction, the relationship between their OH radical rate constant and the amount which reacts can be approximated by Equation (V) above, where the amount reacted will depend on the effective integrated OH radical concentration of the pollution scenario (the INTOH parameter) as well as on the OH radical rate constant. Although use of Equation (V) to estimate reactivities from OH radical rate constants requires an estimate of the INTOH parameter, it should be noted that even a crude guess of INTOH is better than assuming it is zero, which is the assumption implicitly involved in use of the linear kOH method.

If one wishes to derive reactivity scales based on how rapidly a VOC reacts, without regard to a specific effect of its reactions on air quality (such as ozone formation), then it is recommended that "carbon reacted" be utilized as a basis of the scale. This scale would rank VOCs by the number (or mass) of carbon atoms which undergo reaction in the pollution scenario, due to the emissions of a given amount of the VOC. The "carbon reacted" reactivities of the individual VOCs are included in Table 1, and the contributions of the individual VOCs to this measure of reactivity for the various example vehicle emissions are included in Tables 2 and 3 and in the tabulations in the Appendix. Comparisons of these "carbon" reactivities to the ozone reactivities in these tabulations give an indication of the effects of taking differences in reaction mechanisms as they affect ozone into account in the reactivity analysis. Note that if one is concerned with other aspects of air quality besides ozone, such as (for example) oxygenated product formation, estimates of carbon reacted may be a more appropriate measure of reactivity than estimates of ozone formation.

The ozone reactivity analysis of the results of the vehicles emissions tests reported in ARB (1989) indicate that, of the vehicles and fuel combinations tested, the reactivity ranking of the fuels in terms of overall impacts per mile traveled are E85 ~ E95 > Indolene > M100 > M85 > LPG > CNG. This takes both amounts of VOC emitted and VOC reactivity into account. In terms of amounts of ozone formed per gram emitted, the reactivity ranking of the exhaust NMHC emissions from the fuels are Indolene > E95 ~ M85 ~ LPG ~ E85 > M100 > CNG. The reactivity ranking for the evaporative NMHC emissions are Indolene > E95 ~ E85 > M85 > M100.

Of course, these rankings reflect the relative ozone impacts of emissions from these vehicles under the conditions of these tests only, and no conclusions should be drawn concerning the relative ozone benefits resulting from use of these fuels based on these highly limited, and possibly unrepresentative, tests.

In order to develop a more comprehensive analysis of air quality impacts of use of alternative fueled vehicles, it is clear that a much more extensive testing program of vehicle emissions is required. Tests are required from a large number of different using the same type of fuel to obtain an indication the ranges of variability of the emissions, both in

terms of reactivity and total amounts emitted. Once such a data base is available, an ozone reactivity analysis such as that described in this report can then be used to obtain a more comprehensive assessment of the relative ozone impacts of use of different types of alternative fuels can be carried out. Until such an assessment has been carried out, it is premature to judge which, if any, of the possible alternative fuels represents the most promising approach for reducing photochemical smog formation.

ACKNOWLEDGEMENTS

The author wishes to thank Mr. Alvin Lowii, consultant, for many helpful discussions which led to this work, Mr. Larry Osgood of Petrolane Corporation for support of this work and for helpful discussions, Dr. Roger Atkinson of the Air Pollution Research Center for reviewing this draft and for helpful discussions, and Mr. Paul Allen of the California Air Resources Board modeling staff for making the vehicle emissions data available to the author in computer readable form.

Although this report was prepared under funding from the Western Liquid Gas Associations, much of the results discussed herein is due to research being carried out under ongoing research contracts with the U. S. Environmental Protection Agency (Cooperative Agreement No. CR814396-01-0) and the California South Coast Air Quality Management District. However, the opinions and conclusions in this report are entirely those of the author, and do reflect the views and policies of any of these agencies or organizations, nor of the University of California.

REFERENCES

- ARB (1989): "Definition of A Low-Emission Motor Vehicle in Compliance with The Mandates of Health and Safety Code Section 39037.05 (Assembly Bill 234, Leonard, 1987)", Report by Mobile Sources Division, California Air Resources Board, El Monte, California. May 19.
- Atkinson, R. (1986); "Kinetics and Mechanisms of the Gas Phase Reactions of the Hydroxyl Radical with Organic Compounds Under Atmospheric Conditions", Chem Rev., 86, 69-201.
- Atkinson, R. (1987): "A Structure-Activity Relationship for the Estimation of Rate Constants for the Gas-Phase Reactions of OH Radicals with Organic Compounds," Int. J. Chem. Kinet., 19, 799-828.
- Atkinson, R. (1989): "Gas-Phase Tropospheric Chemistry of Organic Compounds: A Review," Atmos. Environ., in press.

- Croes, B. and P. Allen (1989), California Air Resources Board, Sacramento California, private communication.
- Carter, W. P. L. (1988): "Development and Implementation of an Up-To-Date Photochemical Mechanism for Use in Airshed Modeling," Final Report for California Air Resources Board Contract No. A5-122-32, October.
- Carter, W. P. L. and R. Atkinson (1989): "A Computer Modeling Study of Incremental Hydrocarbon Reactivity", Environmental Science and Technology, in press.
- Carter, W. P. L. (1989a): "Estimates of Photochemical Reactivities of Solvent Species Used in Architectural Coatings," presented at the 82nd Annual Meeting of the Air and Waste Management Association, Anaheim California, June 25-30.
- EPA (1984): "Guideline for Using the Carbon Bond Mechanism in City-Specific EKMA," EPA-450/4-84-005, February.
- Carter, W. P. L. (1989b): "A Detailed Mechanism for the Gas-Phase Atmospheric Reactions of Organic Compounds," Atmospheric Environment, in press.
- Gipson, G. L. and W. P. Freas, "Use of City-Specific EKMA in the Ozone RIA", U. S. Environmental Protection Agency, July 1983.
- Lurmann, F. W., W. P. L. Carter, and R. A. Coyner (1987): "A Surrogate Species Chemical Reaction Mechanism for Urban-Scale Air Quality Simulation Models. Volume I - Adaptation of the Mechanism," Final Report, EPA Contract No. 68-02-4104, Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC.
- Russell, A, J. Harris, J. Milford, and D. St.Pierre (1989): "Quantitative Estimate of the Air Quality Impacts of Methanol Fuel Use," Final report, California Air Resources Board Agreement No. A6-048-32, April.
- Weir, B. R., A. S. Rosenbaum, L. A. Gardner, G. Z. Whitten and W. Carter, (1988): "Architectural Coatings in the South Coast Air Basin: Survey, Reactivity, and Toxicity Evaluation", Final Report to the South Coast Management District, SYSAPP-88/137, Systems Applications, Inc. San Rafael, CA, December.

APPENDIX

TABULATIONS OF COMPOSITIONS INDIVIDUAL SPECIES TO PER GRAM REACTIVITIES
OF EXHAUST AND EVAPORATIVE NMHC EMISSIONS

The tables in this Appendix give the results of the detailed speciated analysis of the exhaust and evaporative NMHC emissions from the ARB (1989) tests, taken from Appendix D of that report. These data were provided to the author in computer-readable form by Paul Allen of the ARB modeling staff. The tabulations also show the contributions of each of the chemical species (or groups of species) to the estimated amounts of carbon reacted and to the estimated maximum amounts of ozone formed per gram emitted, derived based on the analysis discussed in the text. The reactivity factors for the individual compounds or groups of compounds are taken from Table 1 of this report. The total reactivity results for these NMHC mixtures are summarized on Table 2.

Table A-1. Chemical Species Reported in Indolene Exhaust NMHC Emissions in the ARB (1989) Tests, and their Contributions to Their Estimated Per-Gram Reactivity.

Description	Weight %	--C Reacted--		-Max. Ozone-	
		(grams)	(%)	(grams)	(%)
Ethane	2.5	0.001	0.2	0.012	0.3
Propane	0.4	0.001	0.1	0.004	0.1
n-Butane	5.5	0.020	3.4	0.103	2.4
Isobutane	0.4	0.001	0.2	0.010	0.2
Branched C5 Alkanes	19.3	0.095	15.9	0.413	9.5
Branched C6 Alkanes	3.8	0.022	3.7	0.087	2.0
2,3-Dimethyl Butane	1.2	0.007	1.2	0.020	0.5
2,2-Dimethyl Butane	0.8	0.002	0.4	0.009	0.2
Branched C7 Alkanes	8.7	0.057	9.6	0.174	4.0
Branched C8 Alkanes	8.1	0.058	9.8	0.139	3.2
Branched C9 Alkanes	0.3	0.002	0.4	0.004	0.1
Branched C10 Alkanes	0.9	0.007	1.1	0.012	0.3
Branched C11 alkanes	1.4	0.011	1.9	0.020	0.5
Cyclopentane	0.2	0.001	0.2	0.008	0.2
Methylcyclopentane	0.5	0.003	0.5	0.018	0.4
C6 Cycloalkanes	3.7	0.027	4.5	0.069	1.6
C7 Cycloalkanes	0.2	0.001	0.2	0.004	0.1
Methylcyclohexane	0.4	0.003	0.5	0.009	0.2
C8 Cycloalkanes	1.5	0.012	2.1	0.042	1.0
Total Alkanes	59.6	0.332	55.9	1.156	26.6
Ethene	3.2	0.026	4.4	0.493	11.3
Propene	2.2	0.019	3.2	0.279	6.4
C4 Alkenes	1.3	0.011	1.9	0.169	3.9
C6 Alkenes	0.5	0.005	0.8	0.041	0.9
Total Alkenes	7.4	0.061	10.3	0.985	22.7
Benzene	2.0	0.005	0.8	0.020	0.5
Toluene	15.6	0.104	17.6	0.828	19.0
Ethyl Benzene	0.8	0.005	0.9	0.040	0.9
n-Propyl Benzene	0.5	0.003	0.5	0.020	0.5
Isopropyl Benzene	0.2	0.002	0.3	0.011	0.2
s-Butyl Benzene	0.2	0.001	0.2	0.008	0.2
o-Xylene	0.9	0.008	1.3	0.096	2.2
m-Xylene	2.1	0.019	3.2	0.252	5.8
Dialkyl Benzenes	1.9	0.017	2.8	0.197	4.5
Trialkyl Benzenes	1.8	0.016	2.7	0.208	4.8
Total Aromatics	26.0	0.181	30.4	1.678	38.6
Acetylene	2.7	0.004	0.7	0.029	0.7
Formaldehyde	2.2	0.009	1.5	0.364	8.4
Acetaldehyde	0.4	0.002	0.4	0.051	1.2
Acrolein	0.5	0.003	0.6	0.067	1.5
Acetone	1.0	0.001	0.2	0.017	0.4
Total Oxygenates	4.2	0.016	2.7	0.498	11.5
Total		0.595		4.347	

Table A-2. Chemical Species Reported in E95 Exhaust NMHC Emissions in the ARB (1989) Tests, and their Contributions to Their Estimated Per-Gram Reactivity.

Description	Weight %	--C Reacted--		-Max. Ozone-	
		(grams)	(%)	(grams)	(%)
Ethane	0.9	0.000	0.1	0.004	0.1
n-Butane	0.2	0.001	0.2	0.003	0.1
n-Heptane	0.1	0.000	0.1	0.001	0.0
Branched C5 Alkanes	1.8	0.009	2.7	0.039	1.1
Branched C6 Alkanes	0.6	0.003	1.0	0.013	0.4
2,3-Dimethyl Butane	0.0	0.000	0.1	0.001	0.0
Branched C7 Alkanes	0.6	0.004	1.2	0.012	0.3
Branched C8 Alkanes	0.8	0.006	1.7	0.014	0.4
Branched C9 Alkanes	0.1	0.001	0.3	0.002	0.1
Branched C10 Alkanes	0.1	0.001	0.3	0.002	0.0
Branched C11 alkanes	0.1	0.001	0.3	0.002	0.0
Methylcyclopentane	0.2	0.001	0.3	0.006	0.2
C6 Cycloalkanes	0.1	0.000	0.1	0.001	0.0
C7 Cycloalkanes	0.1	0.001	0.2	0.002	0.1
Methylcyclohexane	0.1	0.001	0.2	0.002	0.1
C8 Cycloalkanes	0.1	0.000	0.1	0.002	0.0
Total Alkanes	5.8	0.030	9.1	0.106	3.0
Ethene	3.6	0.028	8.6	0.543	15.1
Propene	0.1	0.001	0.2	0.010	0.3
C4 Alkenes	0.0	0.000	0.1	0.003	0.1
C6 Alkenes	0.0	0.000	0.1	0.002	0.1
Total Alkenes	3.7	0.030	8.9	0.558	15.6
Benzene	0.3	0.001	0.2	0.003	0.1
Toluene	0.5	0.003	1.0	0.027	0.8
Ethyl Benzene	0.1	0.001	0.2	0.004	0.1
Isopropyl Benzene	0.0	0.000	0.0	0.001	0.0
s-Butyl Benzene	0.0	0.000	0.0	0.001	0.0
o-Xylene	0.1	0.001	0.3	0.013	0.4
m-Xylene	0.4	0.004	1.2	0.051	1.4
Dialkyl Benzenes	0.3	0.002	0.7	0.028	0.8
Trialkyl Benzenes	0.3	0.003	0.8	0.036	1.0
Total Aromatics	2.1	0.015	4.6	0.164	4.6
Acetylene	1.6	0.002	0.7	0.016	0.5
Ethanol	78.8	0.213	64.2	1.774	49.5
Formaldehyde	1.3	0.005	1.6	0.214	6.0
Acetaldehyde	6.5	0.036	10.7	0.747	20.8
Acrolein	0.0	0.000	0.0	0.003	0.1
Acetone	0.2	0.000	0.1	0.003	0.1
Total Aldehydes/Ketones	8.0	0.041	12.4	0.968	27.0
Total		0.331		3.587	

Table A-3. Chemical Species Reported in E85 Exhaust NMHC Emissions in the ARB (1989) Tests, and their Contributions to Their Estimated Per-Gram Reactivity.

Description	Weight %	--C Reacted--		-Max. Ozone-	
		(grams)	(%)	(grams)	(%)
Ethane	1.1	0.000	0.1	0.005	0.1
Propane	0.1	0.000	0.1	0.001	0.0
n-Butane	0.5	0.002	0.6	0.010	0.3
n-Heptane	0.1	0.001	0.2	0.001	0.0
Branched C5 Alkanes	1.7	0.008	2.4	0.036	1.0
Branched C6 Alkanes	0.7	0.004	1.2	0.016	0.5
2,3-Dimethyl Butane	0.1	0.001	0.2	0.002	0.1
Branched C7 Alkanes	0.9	0.006	1.8	0.018	0.5
Branched C8 Alkanes	2.0	0.015	4.3	0.035	1.0
Branched C9 Alkanes	0.2	0.001	0.4	0.003	0.1
Branched C10 Alkanes	0.1	0.001	0.2	0.001	0.0
Branched C11 alkanes	0.1	0.001	0.3	0.002	0.1
Cyclopentane	0.0	0.000	0.1	0.002	0.0
Methylcyclopentane	0.1	0.001	0.2	0.004	0.1
C7 Cycloalkanes	0.1	0.001	0.1	0.002	0.0
Methylcyclohexane	0.1	0.000	0.1	0.002	0.0
C8 Cycloalkanes	0.1	0.001	0.3	0.003	0.1
Total Alkanes	8.1	0.043	12.8	0.143	4.1
Ethene	3.5	0.028	8.2	0.533	15.4
Propene	0.1	0.001	0.3	0.014	0.4
C4 Alkenes	0.1	0.001	0.2	0.009	0.3
C6 Alkenes	0.0	0.000	0.1	0.003	0.1
Total Alkenes	3.7	0.030	8.8	0.559	16.2
Benzene	0.3	0.001	0.2	0.003	0.1
Toluene	1.6	0.011	3.1	0.085	2.5
Ethyl Benzene	0.2	0.001	0.4	0.009	0.3
o-Xylene	0.2	0.001	0.4	0.017	0.5
m-Xylene	0.4	0.004	1.1	0.052	1.5
Dialkyl Benzenes	0.3	0.002	0.7	0.026	0.8
Trialkyl Benzenes	0.3	0.003	0.9	0.040	1.2
Total Aromatics	3.4	0.024	7.0	0.235	6.8
Acetylene	1.6	0.002	0.7	0.017	0.5
Ethanol	76.8	0.207	61.0	1.728	50.0
Formaldehyde	1.0	0.004	1.2	0.172	5.0
Acetaldehyde	5.1	0.028	8.3	0.595	17.2
Acrolein	0.0	0.000	0.1	0.005	0.1
Acetone	0.2	0.000	0.1	0.003	0.1
Total Aldehydes/Ketones	6.4	0.033	9.7	0.774	22.4
Total		0.340		3.456	

Table A-4. Chemical Species Reported in M85 Exhaust NMHC Emissions in the ARB (1989) Tests, and their Contributions to Their Estimated Per-Gram Reactivity.

Description	Weight %	--C Reacted--		-Max. Ozone-	
		(grams)	(%)	(grams)	(%)
Ethane	0.5	0.000	0.1	0.002	0.1
n-Butane	2.0	0.007	2.8	0.037	1.1
n-Heptane	0.2	0.001	0.5	0.002	0.1
Branched C5 Alkanes	2.9	0.014	5.5	0.061	1.7
Branched C6 Alkanes	1.6	0.010	3.8	0.038	1.1
2,3-Dimethyl Butane	0.3	0.002	0.6	0.004	0.1
2,2-Dimethyl Butane	0.2	0.000	0.2	0.002	0.1
Branched C7 Alkanes	1.9	0.012	4.8	0.037	1.1
Branched C8 Alkanes	7.4	0.053	20.9	0.127	3.6
Branched C9 Alkanes	0.5	0.003	1.4	0.007	0.2
Branched C10 Alkanes	0.2	0.001	0.5	0.002	0.1
Branched C11 alkanes	0.2	0.002	0.6	0.003	0.1
Cyclopentane	0.1	0.001	0.2	0.003	0.1
Methylcyclopentane	0.1	0.000	0.2	0.003	0.1
C6 Cycloalkanes	0.1	0.001	0.2	0.002	0.0
C7 Cycloalkanes	0.1	0.001	0.2	0.002	0.1
Methylcyclohexane	0.1	0.001	0.3	0.002	0.1
C8 Cycloalkanes	0.3	0.002	0.8	0.007	0.2
Total Alkanes	18.4	0.112	43.7	0.344	9.8
Ethene	0.7	0.005	2.1	0.102	2.9
Propene	0.3	0.002	0.9	0.034	1.0
C4 Alkenes	0.4	0.003	1.3	0.047	1.3
C6 Alkenes	0.1	0.001	0.4	0.008	0.2
Total Alkenes	1.4	0.012	4.6	0.192	5.5
Benzene	0.9	0.002	0.8	0.009	0.2
Toluene	1.1	0.007	2.8	0.057	1.6
Ethyl Benzene	0.4	0.003	1.1	0.020	0.6
n-Propyl Benzene	0.2	0.001	0.5	0.008	0.2
s-Butyl Benzene	0.1	0.001	0.2	0.003	0.1
o-Xylene	0.3	0.003	1.0	0.032	0.9
m-Xylene	1.0	0.009	3.5	0.119	3.4
Dialkyl Benzenes	1.0	0.009	3.3	0.100	2.8
Trialkyl Benzenes	1.3	0.011	4.4	0.144	4.1
Total Aromatics	6.1	0.045	17.8	0.493	14.1
Acetylene	0.3	0.000	0.2	0.003	0.1
Methanol	63.3	0.045	17.6	0.887	25.3
Formaldehyde	9.1	0.036	14.2	1.493	42.6
Acetaldehyde	0.6	0.003	1.2	0.065	1.9
Acrolein	0.1	0.001	0.3	0.017	0.5
Acetone	0.5	0.001	0.3	0.009	0.3
Total Aldehyde/Ketones	10.3	0.041	16.1	1.584	45.2
Total		0.255		3.503	

Table A-5. Chemical Species Reported in M100 Exhaust NMHC Emissions in the ARB (1989) Tests, and their Contributions to Their Estimated Per-Gram Reactivity.

Description	Weight %	--C Reacted--		-Max. Ozone-	
		(grams)	(%)	(grams)	(%)
Propane	0.0	0.000	0.1	0.000	0.0
n-Butane	0.1	0.000	0.2	0.001	0.1
n-Heptane	0.1	0.000	0.4	0.001	0.0
Isobutane	0.0	0.000	0.1	0.001	0.0
Branched C5 Alkanes	0.3	0.002	1.5	0.007	0.3
Branched C6 Alkanes	0.3	0.001	1.4	0.006	0.2
2,3-Dimethyl Butane	0.0	0.000	0.2	0.000	0.0
Branched C7 Alkanes	0.3	0.002	1.9	0.006	0.3
Branched C8 Alkanes	0.3	0.002	2.1	0.005	0.2
Branched C9 Alkanes	0.1	0.001	0.8	0.002	0.1
Methylcyclopentane	0.0	0.000	0.2	0.001	0.1
C6 Cycloalkanes	0.0	0.000	0.1	0.000	0.0
C7 Cycloalkanes	0.1	0.000	0.4	0.001	0.1
Methylcyclohexane	0.0	0.000	0.2	0.001	0.0
C8 Cycloalkanes	0.0	0.000	0.2	0.001	0.0
Total Alkanes	1.8	0.011	9.9	0.035	1.4
Ethene	0.1	0.001	0.5	0.010	0.4
Propene	0.0	0.000	0.1	0.002	0.1
C4 Alkenes	0.0	0.000	0.1	0.001	0.1
C6 Alkenes	0.0	0.000	0.2	0.002	0.1
Total Alkenes	0.1	0.001	0.9	0.016	0.7
Benzene	0.1	0.000	0.2	0.001	0.0
Toluene	0.6	0.004	3.7	0.032	1.3
Ethyl Benzene	0.0	0.000	0.1	0.001	0.0
o-Xylene	0.0	0.000	0.4	0.005	0.2
m-Xylene	0.1	0.001	0.7	0.010	0.4
Dialkyl Benzenes	0.1	0.001	0.7	0.008	0.3
Trialkyl Benzenes	0.1	0.001	0.9	0.013	0.5
Total Aromatics	1.0	0.007	6.7	0.070	2.9
Acetylene	0.0	0.000	0.1	0.001	0.0
Methanol	90.6	0.064	58.9	1.268	52.1
Formaldehyde	6.3	0.025	23.0	1.034	42.5
Acetaldehyde	0.1	0.000	0.4	0.009	0.4
Acetone	0.1	0.000	0.1	0.001	0.1
Total Aldehyde/Ketones	6.4	0.026	23.5	1.045	42.9
Total		0.109		2.435	

Table A-6. Chemical Species Reported in LPG Exhaust NMHC Emissions in the ARB (1989) Tests, and their Contributions to Their Estimated Per-Gram Reactivity.

Description	Weight %	--C Reacted--		-Max. Ozone-	
		(grams)	(%)	(grams)	(%)
Ethane	4.4	0.002	0.7	0.022	0.6
Propane	70.6	0.141	46.0	0.706	19.9
n-Butane	0.8	0.003	1.0	0.015	0.4
Isobutane	1.5	0.005	1.6	0.036	1.0
Branched C5 Alkanes	0.9	0.004	1.4	0.019	0.5
Branched C6 Alkanes	0.2	0.001	0.3	0.004	0.1
Branched C7 Alkanes	0.3	0.002	0.6	0.005	0.2
Branched C8 Alkanes	0.4	0.003	1.0	0.007	0.2
Branched C9 Alkanes	0.0	0.000	0.1	0.000	0.0
Branched C10 Alkanes	0.2	0.001	0.4	0.002	0.1
Branched C11 alkanes	0.1	0.001	0.4	0.002	0.1
Cyclopentane	0.0	0.000	0.1	0.002	0.0
Methylcyclopentane	0.0	0.000	0.0	0.001	0.0
C6 Cycloalkanes	0.0	0.000	0.1	0.001	0.0
C7 Cycloalkanes	0.1	0.001	0.2	0.002	0.1
Methylcyclohexane	0.1	0.001	0.4	0.004	0.1
Total Alkanes	79.8	0.167	54.4	0.829	23.4
Ethene	7.8	0.062	20.2	1.183	33.4
Propene	4.9	0.042	13.6	0.616	17.4
C4 Alkenes	1.0	0.009	2.8	0.125	3.5
C6 Alkenes	0.0	0.000	0.1	0.002	0.1
Total Alkenes	13.6	0.113	36.7	1.927	54.4
Benzene	0.2	0.000	0.1	0.002	0.1
Toluene	0.6	0.004	1.2	0.030	0.8
Ethyl Benzene	0.0	0.000	0.1	0.002	0.1
n-Propyl Benzene	0.0	0.000	0.0	0.001	0.0
o-Xylene	0.1	0.001	0.2	0.009	0.2
m-Xylene	0.0	0.000	0.1	0.003	0.1
Trialkyl Benzenes	0.1	0.001	0.4	0.015	0.4
Total Aromatics	1.0	0.007	2.2	0.061	1.7
Acetylene	0.8	0.001	0.4	0.008	0.2
Formaldehyde	3.9	0.016	5.1	0.641	18.1
Acetaldehyde	0.5	0.003	0.9	0.059	1.7
Acrolein	0.1	0.001	0.2	0.013	0.4
Acetone	0.2	0.000	0.1	0.003	0.1
Total Oxygenates	4.7	0.019	6.3	0.716	20.2
Total		0.307		3.541	

Table A-7. Chemical Species Reported in CNG Exhaust NMHC Emissions in the ARB (1989) Tests, and their Contributions to Their Estimated Per-Gram Reactivity.

Description	Weight %	--C Reacted--		-Max. Ozone-	
		(grams)	(%)	(grams)	(%)
Ethane	71.8	0.034	19.5	0.352	18.5
Propane	8.1	0.016	9.3	0.081	4.3
n-Butane	0.6	0.002	1.1	0.010	0.5
n-Heptane	0.1	0.001	0.4	0.001	0.1
Isobutane	0.3	0.001	0.5	0.006	0.3
Branched C5 Alkanes	2.1	0.010	5.9	0.045	2.3
Branched C6 Alkanes	1.5	0.009	5.1	0.035	1.8
2,3-Dimethyl Butane	0.4	0.002	1.4	0.006	0.3
2,2-Dimethyl Butane	0.0	0.000	0.1	0.001	0.0
Branched C7 Alkanes	1.3	0.009	5.0	0.026	1.4
Branched C8 Alkanes	1.4	0.010	5.8	0.024	1.3
Branched C9 Alkanes	0.1	0.001	0.5	0.002	0.1
Cyclopentane	0.1	0.000	0.2	0.002	0.1
Methylcyclopentane	0.6	0.004	2.3	0.022	1.2
C6 Cycloalkanes	0.1	0.000	0.2	0.001	0.1
C7 Cycloalkanes	0.1	0.000	0.3	0.001	0.1
Methylcyclohexane	0.1	0.001	0.5	0.003	0.1
C8 Cycloalkanes	0.1	0.001	0.3	0.002	0.1
Total Alkanes	88.6	0.101	58.4	0.620	32.7
Ethene	1.7	0.014	7.8	0.257	13.6
Propene	2.6	0.023	13.0	0.331	17.4
C4 Alkenes	0.1	0.001	0.3	0.008	0.4
C6 Alkenes	0.4	0.003	1.8	0.027	1.4
Total Alkenes	4.7	0.040	22.9	0.625	32.9
Benzene	0.9	0.002	1.3	0.009	0.5
Toluene	0.6	0.004	2.2	0.030	1.6
Ethyl Benzene	0.1	0.001	0.3	0.004	0.2
o-Xylene	0.3	0.003	1.7	0.036	1.9
m-Xylene	0.6	0.005	3.1	0.071	3.8
Dialkyl Benzenes	0.1	0.001	0.3	0.006	0.3
Trialkyl Benzenes	0.4	0.004	2.3	0.050	2.6
Total Aromatics	3.0	0.019	11.1	0.207	10.9
Acetylene	0.1	0.000	0.0	0.001	0.0
Formaldehyde	2.3	0.009	5.3	0.381	20.0
Acetaldehyde	0.5	0.003	1.4	0.053	2.8
Acetone	0.8	0.001	0.7	0.014	0.7
Total Oxygenates	3.6	0.013	7.5	0.447	23.5
Total		0.173		1.900	

Table A-8. Chemical Species Reported in Indolene Evaporative NMHC Emissions in the ARB (1989) Tests, and their Contributions to Their Estimated Per-Gram Reactivity.

Description	Weight %	--C Reacted--		-Max. Ozone-	
		(grams)	(%)	(grams)	(%)
Propane	0.6	0.001	0.2	0.006	0.2
n-Butane	11.2	0.040	6.4	0.207	6.0
n-Heptane	1.0	0.006	1.0	0.011	0.3
Isobutane	0.5	0.002	0.3	0.012	0.4
Branched C5 Alkanes	17.2	0.084	13.4	0.369	10.7
Branched C6 Alkanes	5.5	0.032	5.1	0.127	3.7
2,3-Dimethyl Butane	1.4	0.008	1.3	0.022	0.6
Branched C7 Alkanes	8.2	0.054	8.6	0.165	4.8
Branched C8 Alkanes	21.9	0.158	25.0	0.374	10.8
Branched C9 Alkanes	2.0	0.015	2.4	0.030	0.9
Branched C10 Alkanes	0.9	0.007	1.1	0.012	0.4
Branched C11 alkanes	0.2	0.002	0.3	0.004	0.1
Methylcyclopentane	0.6	0.004	0.6	0.022	0.6
C6 Cycloalkanes	0.3	0.002	0.3	0.005	0.1
C7 Cycloalkanes	1.2	0.009	1.4	0.029	0.8
Methylcyclohexane	0.5	0.004	0.6	0.012	0.3
C8 Cycloalkanes	0.7	0.006	0.9	0.020	0.6
Total Alkanes	73.8	0.434	68.8	1.427	41.3
Ethene	0.0	0.000	0.1	0.007	0.2
Propene	0.0	0.000	0.0	0.001	0.0
C4 Alkenes	0.3	0.003	0.4	0.038	1.1
C6 Alkenes	0.1	0.001	0.2	0.011	0.3
Total Alkenes	0.5	0.004	0.7	0.057	1.6
Benzene	1.0	0.002	0.4	0.010	0.3
Toluene	10.0	0.067	10.6	0.532	15.4
Ethyl Benzene	2.9	0.020	3.2	0.148	4.3
n-Propyl Benzene	0.4	0.003	0.4	0.016	0.5
Isopropyl Benzene	0.3	0.002	0.3	0.013	0.4
o-Xylene	1.6	0.014	2.2	0.175	5.1
m-Xylene	5.7	0.051	8.1	0.672	19.5
Dialkyl Benzenes	1.6	0.015	2.3	0.170	4.9
Trialkyl Benzenes	2.0	0.018	2.8	0.229	6.6
Total Aromatics	25.5	0.192	30.4	1.965	56.9
Acetylene	0.2	0.000	0.0	0.002	0.1
Total		0.631		3.450	

Table A-9. Chemical Species Reported in E95 Evaporative NMHC Emissions in the ARB (1989) Tests, and their Contributions to Their Estimated Per-Gram Reactivity.

Description	Weight %	--C Reacted--		-Max. Ozone-	
		(grams)	(%)	(grams)	(%)
Propane	0.2	0.000	0.1	0.002	0.1
n-Butane	5.4	0.020	5.5	0.101	4.0
n-Heptane	0.5	0.003	0.9	0.006	0.2
Isobutane	1.0	0.004	1.0	0.025	1.0
Branched C5 Alkanes	10.9	0.053	15.0	0.233	9.3
Branched C6 Alkanes	1.5	0.009	2.5	0.034	1.4
2,3-Dimethyl Butane	0.2	0.001	0.4	0.004	0.1
2,2-Dimethyl Butane	0.0	0.000	0.0	0.001	0.0
Branched C7 Alkanes	2.1	0.014	3.9	0.042	1.7
Branched C8 Alkanes	2.8	0.020	5.7	0.048	1.9
Cyclopentane	0.0	0.000	0.0	0.001	0.0
Methylcyclopentane	0.5	0.004	1.0	0.020	0.8
C6 Cycloalkanes	0.0	0.000	0.1	0.001	0.0
C7 Cycloalkanes	0.0	0.000	0.1	0.001	0.0
Methylcyclohexane	0.3	0.002	0.7	0.008	0.3
C8 Cycloalkanes	0.2	0.001	0.4	0.005	0.2
Total Alkanes	25.8	0.132	37.3	0.530	21.2
Ethene	0.3	0.002	0.7	0.045	1.8
Propene	0.1	0.001	0.3	0.016	0.6
C4 Alkenes	0.2	0.002	0.5	0.026	1.0
Total Alkenes	0.6	0.005	1.5	0.086	3.5
Benzene	1.1	0.003	0.7	0.011	0.4
Toluene	1.1	0.007	2.1	0.059	2.3
Ethyl Benzene	0.2	0.002	0.5	0.012	0.5
o-Xylene	0.0	0.000	0.0	0.001	0.0
m-Xylene	1.8	0.016	4.5	0.213	8.5
Dialkyl Benzenes	0.3	0.003	0.9	0.036	1.4
Trialkyl Benzenes	0.1	0.001	0.4	0.017	0.7
Total Aromatics	4.7	0.032	9.1	0.347	13.9
Acetylene	0.6	0.001	0.2	0.006	0.2
Ethanol	68.2	0.184	51.9	1.535	61.3
Total		0.355		2.506	

Table A-10. Chemical Species Reported in E85 Evaporative NMHC Emissions in the ARB (1989) Tests, and their Contributions to Their Estimated Per-Gram Reactivity.

Description	Weight %	--C Reacted--		-Max. Ozone-	
		(grams)	(%)	(grams)	(%)
Propane	0.3	0.001	0.2	0.003	0.1
n-Butane	2.5	0.009	2.6	0.046	1.8
n-Heptane	0.2	0.002	0.4	0.003	0.1
Isobutane	0.2	0.001	0.2	0.004	0.2
Branched C5 Alkanes	5.4	0.026	7.7	0.116	4.5
Branched C6 Alkanes	0.8	0.005	1.4	0.019	0.8
2,3-Dimethyl Butane	0.1	0.001	0.2	0.002	0.1
2,2-Dimethyl Butane	0.1	0.000	0.1	0.001	0.1
Branched C7 Alkanes	1.6	0.011	3.1	0.033	1.3
Branched C8 Alkanes	2.4	0.017	5.0	0.041	1.6
Branched C9 Alkanes	0.4	0.003	0.8	0.006	0.2
Branched C10 Alkanes	0.1	0.001	0.2	0.001	0.1
Branched C11 alkanes	0.2	0.002	0.5	0.003	0.1
Cyclopentane	0.1	0.001	0.2	0.005	0.2
Methylcyclopentane	0.2	0.001	0.3	0.007	0.3
C6 Cycloalkanes	0.1	0.001	0.2	0.002	0.1
Methylcyclohexane	0.3	0.002	0.7	0.008	0.3
C8 Cycloalkanes	0.2	0.002	0.5	0.005	0.2
Total Alkanes	15.3	0.084	24.5	0.305	11.9
C4 Alkenes	0.1	0.001	0.2	0.012	0.5
C6 Alkenes	0.0	0.000	0.0	0.001	0.0
Total Alkenes	0.1	0.001	0.3	0.013	0.5
Benzene	0.2	0.000	0.1	0.002	0.1
Toluene	3.2	0.022	6.3	0.172	6.7
Ethyl Benzene	0.1	0.001	0.2	0.006	0.2
n-Propyl Benzene	0.1	0.001	0.3	0.006	0.2
Isopropyl Benzene	0.1	0.001	0.2	0.005	0.2
s-Butyl Benzene	0.0	0.000	0.0	0.001	0.0
o-Xylene	0.5	0.005	1.3	0.057	2.2
m-Xylene	0.7	0.006	1.8	0.083	3.3
Dialkyl Benzenes	0.7	0.006	1.9	0.075	2.9
Trialkyl Benzenes	0.6	0.005	1.5	0.067	2.6
Total Aromatics	6.4	0.047	13.8	0.474	18.6
Acetylene	0.2	0.000	0.1	0.002	0.1
Ethanol	78.0	0.211	61.3	1.755	68.9
Total		0.343		2.549	

Table A-11. Chemical Species Reported in M85 Evaporative NMHC Emissions in the ARB (1989) Tests, and their Contributions to Their Estimated Per-Gram Reactivity.

Description	Weight %	--C Reacted--		-Max. Ozone-	
		(grams)	(%)	(grams)	(%)
Propane	0.2	0.000	0.1	0.002	0.1
n-Butane	8.2	0.029	11.2	0.151	7.6
n-Heptane	0.7	0.005	1.7	0.008	0.4
Isobutane	0.9	0.003	1.2	0.022	1.1
Branched C5 Alkanes	10.6	0.052	19.7	0.226	11.3
Branched C6 Alkanes	2.5	0.015	5.6	0.057	2.9
2,3-Dimethyl Butane	0.6	0.004	1.3	0.010	0.5
Branched C7 Alkanes	2.6	0.017	6.6	0.052	2.6
Branched C8 Alkanes	2.3	0.017	6.4	0.040	2.0
Branched C9 Alkanes	0.1	0.001	0.3	0.002	0.1
Branched C10 Alkanes	0.1	0.001	0.4	0.002	0.1
Branched C11 alkanes	1.4	0.011	4.2	0.020	1.0
Cyclopentane	0.3	0.002	0.8	0.014	0.7
Methylcyclopentane	0.6	0.004	1.5	0.022	1.1
C6 Cycloalkanes	0.4	0.003	1.0	0.007	0.3
C7 Cycloalkanes	0.2	0.001	0.4	0.004	0.2
Methylcyclohexane	0.3	0.003	1.0	0.008	0.4
C8 Cycloalkanes	0.2	0.002	0.7	0.007	0.3
Total Alkanes	32.2	0.169	64.3	0.653	32.7
Ethene	0.0	0.000	0.0	0.001	0.1
C4 Alkenes	0.5	0.005	1.8	0.069	3.4
C6 Alkenes	0.1	0.001	0.2	0.005	0.3
Total Alkenes	0.6	0.005	2.0	0.075	3.8
Benzene	1.0	0.002	0.9	0.010	0.5
Toluene	3.7	0.025	9.5	0.198	9.9
Ethyl Benzene	0.2	0.001	0.5	0.010	0.5
s-Butyl Benzene	0.0	0.000	0.1	0.001	0.0
o-Xylene	0.5	0.005	1.7	0.056	2.8
m-Xylene	0.4	0.004	1.5	0.052	2.6
Dialkyl Benzenes	0.3	0.002	0.9	0.029	1.4
Trialkyl Benzenes	0.6	0.005	2.1	0.069	3.4
Total Aromatics	6.8	0.045	17.3	0.425	21.3
Acetylene	0.1	0.000	0.1	0.001	0.1
Methanol	60.3	0.043	16.3	0.844	42.2
Total		0.262		1.998	

Table A-12. Chemical Species Reported in M100 Evaporative NMHC Emissions in the ARB (1989) Tests, and their Contributions to Their Estimated Per-Gram Reactivity.

Description	Weight %	--C Reacted--		-Max. Ozone-	
		(grams)	(%)	(grams)	(%)
n-Butane	0.2	0.001	0.7	0.004	0.2
n-Heptane	0.1	0.001	0.7	0.001	0.1
Isobutane	0.0	0.000	0.1	0.001	0.0
Branched C5 Alkanes	1.4	0.007	6.2	0.031	1.9
Branched C6 Alkanes	0.5	0.003	2.8	0.013	0.8
2,3-Dimethyl Butane	0.0	0.000	0.2	0.001	0.0
2,2-Dimethyl Butane	0.0	0.000	0.1	0.000	0.0
Branched C7 Alkanes	0.3	0.002	2.0	0.007	0.4
Branched C8 Alkanes	0.7	0.005	4.7	0.013	0.8
Branched C9 Alkanes	0.0	0.000	0.2	0.000	0.0
Branched C10 Alkanes	0.0	0.000	0.2	0.000	0.0
Cyclopentane	0.1	0.000	0.3	0.002	0.1
Methylcyclopentane	0.2	0.001	1.2	0.008	0.5
C6 Cycloalkanes	0.1	0.000	0.4	0.001	0.1
C7 Cycloalkanes	0.1	0.001	0.8	0.003	0.2
Methylcyclohexane	0.1	0.001	0.8	0.003	0.2
C8 Cycloalkanes	0.1	0.000	0.4	0.001	0.1
Total Alkanes	4.2	0.025	21.5	0.089	5.4
Propene	0.0	0.000	0.1	0.002	0.1
C4 Alkenes	0.2	0.002	1.5	0.025	1.5
Total Alkenes	0.2	0.002	1.6	0.027	1.7
Benzene	0.4	0.001	0.8	0.004	0.2
Toluene	1.1	0.007	6.3	0.057	3.5
Ethyl Benzene	0.2	0.001	1.1	0.010	0.6
Isopropyl Benzene	0.0	0.000	0.2	0.001	0.1
o-Xylene	0.2	0.002	1.9	0.027	1.6
m-Xylene	0.9	0.008	6.9	0.105	6.4
Dialkyl Benzenes	0.1	0.001	0.8	0.011	0.7
Trialkyl Benzenes	0.3	0.002	2.0	0.030	1.8
Total Aromatics	3.2	0.023	20.0	0.245	14.8
Acetylene	0.1	0.000	0.1	0.001	0.0
Methanol	92.3	0.066	56.8	1.293	78.1
Total		0.115		1.655	