California's Hydrocarbon Reactivity Experience

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1. INTRODUCTION

Despite the progress made over the past 30 years, California still has some of the dirtiest air in the United States. The enjoyable climate of constant sunshine and warm temperatures ensures that many people choose to live in the state. The population of California has grown at an annual rate about twice that of the other 49 states, and this trend is expected to continue. Additionally, the unique topography of large basins surrounded by mountains and the presence of meteorological conditions conducive to formation of emissions-trapping inversion layers creates ideal conditions for high pollutant concentrations. However, notwithstanding the large increases in mobile and stationary sources, California's air quality has shown steady improvements since the early 1970's due to hydrocarbon (HC) and nitrogen oxides (NO_x) controls. Figure 1 shows the reduction in the annual maximum hour ozone concentrations in the Los Angeles area since 1965.

This success of California's policy of controlling HC and NO_x has been tied to aggressive and innovative control strategies based on standard command and control designs. Recently, a new paradigm has emerged that recognizes that more than one control method may exist to gain the required benefits, and that flexibility in control strategies should be emphasized. Hydrocarbon reactivity, or ozone production potential,

is one such concept that has received and is receiving increased attention for the control of ozone. In this paper, reactivity and California's experience in implementing the concept into control strategies, plans, and regulations is explored.

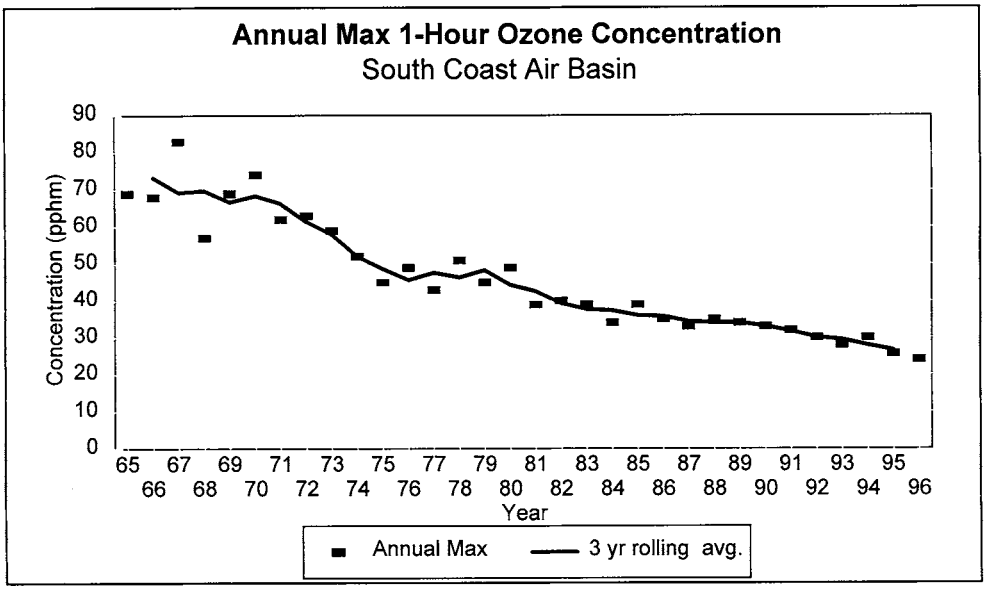

Figure 1. Trend of annual maximum ozone concentrations in South Coast Air Basin.

2. HYDROCARBON REACTIVITY

The amount of ozone formed in the atmosphere due to the reactions of a specific hydrocarbon defines its reactivity or ozone production potential. The earliest studies of photochemical air pollution showed that the amount of ozone formed was dependent on the nature of the organic compounds initially present (Haagen-Smit et al., 1953). The first reactivity scale grew out of these studies, in which organic compounds were ranked by their ozone-forming ability. In the mid-1970's a reactivity scale based on the rate at which a hydrocarbon reacts with the hydroxyl (OH) radical was developed in recognition of the importance that OH radical/hydrocarbon reactions had on ozone formation

(Darnell et al., 1976; and Wu et al., 1976). However, the OH radical reactivity scale is based only on the first of many reactions a hydrocarbon will be involved in before ozone is formed. The subsequent reactions will also depend on the mixture of hydrocarbons in the atmosphere. To take these remaining reactions into account, the reactivity of a hydrocarbon was defined to consist of two parts -- kinetic reactivity and mechanistic reactivity (Carter and Atkinson, 1989; Carter 1994). The kinetic portion is based on the OH radical reaction rate. The mechanistic portion takes into account the subsequent reactions the molecule undergoes with and how much additional ozone is formed because of these reactions. In general a hydrocarbon's reactivity depends on three factors: 1) how rapidly it reacts (kinetic reactivity); 2) the nature of its reaction mechanism (mechanistic reactivity); and 3) the type of environment into which it is emitted (a factor in both kinetic and mechanistic reactivity).

3. HYDROCARBON REACTIVITY AND REGULATIONS

Incorporation of reactivity into California's Low-Emission Vehicles/Clean Fuels (LEV/CF) regulations began in 1987 with the formation of the Advisory Board on Air Quality and Fuels. The Advisory Board's mandate was to define a low-emission vehicle that either was fueled by conventional gasoline and had hydrocarbon exhaust mass emissions equal to half of the existing standard for new cars, or operated on an alternative fuel with an equivalent or lower effect on ozone formation. The staff of the California Air Resources Board recommended that the reactivity of the exhaust emissions be used as the basis for comparing the air quality impacts of the various fuels. Reactivity adjustment factors (RAF's) were developed and adopted as a part of the regulation.

The RAF is defined as the ratio of the reactivity of the low-emission vehicle operated on the alternative fuel to the reactivity of the low-emission vehicle operated on conventional gasoline. Because the reactivity concept was to be adopted into the regulation, it had to withstand scientific and legal scrutiny. The remainder of this paper describes the technical issues that were addressed before the concept of reactivity could be formally adopted, the areas where reactivity may be used in the future, and the research focused

on refining the reactivity concept.

4. DEFINITION OF HYDROCARBON REACTIVITY

Perhaps the most fundamental technical question concerning reactivity is how should reactivity be defined. The most relevant definition (from a regulatory perspective) of reactivity would be the change in ozone in the region of concern caused by a change in the emissions of the hydrocarbon being regulated. However, this definition is not very practical because the value calculated is affected by changes in the quantities emitted of the compound being studied. To avoid this dependence, an incremental reactivity value is typically used. Incremental reactivity is defined as the change in the amount of ozone caused by an incremental change in the amount of the compound's emissions divided by the incremental change in the amount of the compound's emissions (i.e., the partial derivative of amount of ozone with respect to the change in amount of the compound of interest). This definition for incremental reactivity takes into account all aspects of the compound's reaction mechanism and the effects of the other compounds present in the region, and was determined to represent a more comprehensive measure of the effect a hydrocarbon would have on ozone formation (Carter and Atkinson, 1989; and Lowi and Carter, 1990).

Ultimately, the maximum incremental reactivity (MIR) was chosen as the value to be used in the LEV/CF regulations because it is defined where hydrocarbon controls would be most effective. Figure 2 shows a plot of incremental reactivity versus the hydrocarbon-to-NO_x ratio.

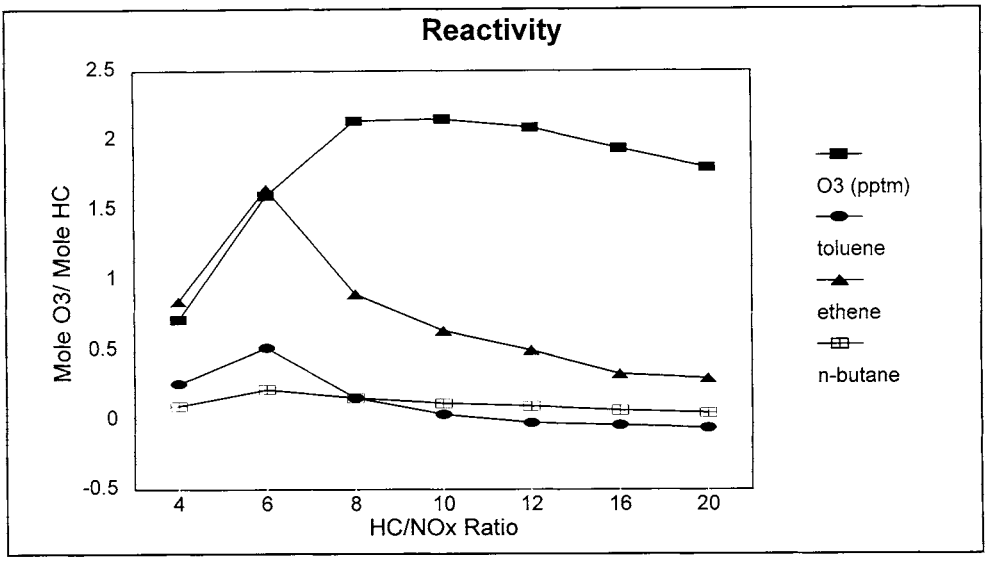

Figure 2. Incremental reactivity of selected hydrocarbons.

The y-axis corresponds to amount of ozone formed per addition of the three compounds plotted (toluene, ethene, and n-butane). As mentioned above, the incremental reactivity depends on the mixture into which the hydrocarbon is emitted. An important parameter of the mixture is the amount of NO_x present relative to the amount of hydrocarbons present. This is typically represented by the ratio of hydrocarbons to NO_x (HC/NO_x). The MIR values occur at HC/NO_x ratios where the incremental reactivities are at their maximum, and, coincidentally, the HC/NO_x ratios where this occurs are very close to the ratios found in typical urban environments in the United States. Controls based on the MIR values correspond to conditions where changes in hydrocarbon emissions have their greatest effect on ozone concentrations, and because the MIR values are defined at HC/NO_x ratios similar to the ambient levels found in major urban areas, the MIR values are particularly relevant to control plans for California cities. California control plans have always favored both hydrocarbon controls, which are more effective in low

HC/NO_x areas (i.e., cities), and NOx controls, which are necessary in high HC/NO_x areas downwind of urban centers, to improve the air quality. Using the MIR scale complements this approach by emphasizing the benefits of hydrocarbon controls in areas especially sensitive to them.

Returning to Figure 2, some other characteristics of hydrocarbon reactivities can be seen. The relative reactivities of the major groups of compounds are illustrated. The olefins (alkenes) are the most reactive, followed by the aromatic compounds (toluene) with the saturated hydrocarbons (alkanes) the least reactive. The peak or maximum incremental reactivity is easily seen at a HC/NOx ratio of around 6, and the difference between the compound reactivities drops off quickly at ratio values greater than 6. The *relative* reactivity of each type of compound stays the same because the reactivities rise and fall together. Toluene is atypical in that its incremental reactivity value drops below that of the alkanes and becomes negative. This is the result of NO_x sinks in the aromatic reaction mechanisms.

Incremental reactivities of compounds cannot be easily measured. Typically, the values are determined from computer models that simulate atmospheric conditions (Carter and Atkinson 1989; Bergin et al., 1995; Carter 1994), and the values are validated by appropriately planned experimental chamber studies (Carter et al. 1995). Computer models have inherent uncertainties because of approximations made in developing the models, and the inputs used in the models. Moreover, uncertainties are introduced from environmental chamber experiments because it is difficult to exactly simulate the ambient environment. Addressing and reducing these uncertainties was necessary before the concept of reactivity could be used in a regulation.

5. REACTIVITY SCALE UNCERTAINTIES

Many factors contribute to the uncertainty of the reactivity value determined for any hydrocarbon, and a reactivity value containing large uncertainties is of no use for developing and implementing a regulation. Uncertainty in the MIR values is introduced by the chamber experiments used to validate chemical mechanisms and estimate

reactivity values, the choice of environmental conditions used in the models used to calculate MIR values, and the assumptions used in developing the chemical mechanisms. For the reactivity adjustment factors used in the LEV/CF regulations, the variability of the hydrocarbon exhaust emissions from mobile sources introduces additional uncertainties. These uncertainties and how the uncertainties were addressed are described below.

Environmental chamber experiments are used (1) to estimate the reactivities of the compounds of concern and (2) to validate chemical mechanisms use to model the relevant atmospheric chemistry (Carter and Atkinson, 1989; Carter et al., 1995, Carter and Lurmann, 1991). Chamber-derived reactivity values are not expected to well represent actual values because of chamber effects such as radical generation on the walls, and more important, the choice of an appropriate hydrocarbon mixture for the chamber run. Reactivity values are affected by the nature of the ambient atmosphere, and the choice of the hydrocarbon mixture limits the usefulness of these derived reactivity values to areas where the chamber mixture represents the actual atmosphere.

A more important concern is the appropriateness of the environmental conditions assumed in the modeling runs used to calculate MIR values. Ideally, the reactivity value would be applicable to all environmental conditions found in any region where ozone control plans are needed. An unfortunate limitation of any reactivity definition is that both the absolute and the relative reactivity values change with different environmental conditions (different hydrocarbon mixtures and different hydrocarbon-to-NO_x ratios). Therefore, no reactivity scale can be expected to accurately represent all environmental conditions.

In developing the MIR values incorporated into the LEV/CF regulations, the issue of variable environmental conditions was addressed by using an average of the environmental conditions found in 39 cities in the United States. To further reduce variability, a normalized reactivity value was defined by dividing the hydrocarbon's reactivity value by a total-species-weighted-average reactivity based on all the hydrocarbon species in the specific city and multiplying by the 39-city average of the total species-weighted average reactivity of all the cities. The normalized version of the MIR reduced the variability from about 20% to 12%.

Bergin et al. (1995) compare the MIR values generated by Carter (1994) who used a box model to represent the atmospheric conditions, to the MIR values calculated with a much more sophisticated urban airshed model (the Carnegie/California Institute of Technology (CIT) Model). The urban airshed model incorporates the spatial variations in the hydrocarbon and NO_x concentrations. As mentioned above, the MIR values are very sensitive to the hydrocarbon-to-NO_x ratio, and the use of the more sophisticated airshed model gives an indication of the magnitude of the effect of these spatial variations on the MIR value.

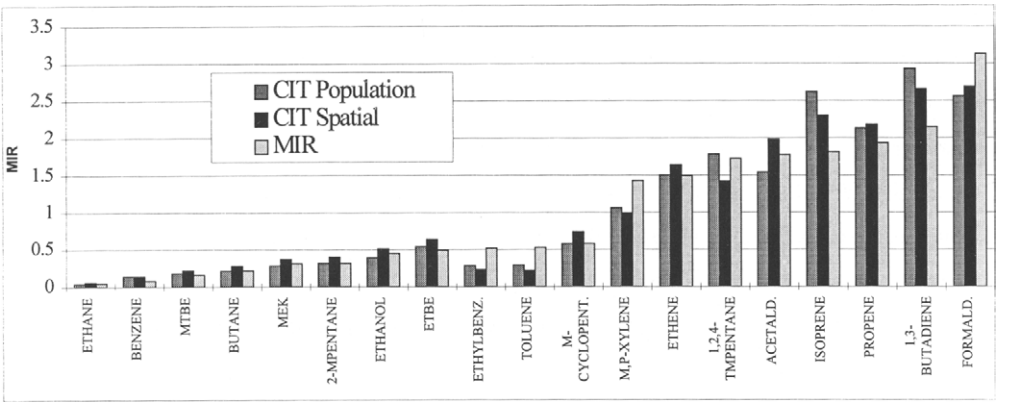

Figure 3. Comparison of Carter's MIR values to those calculated from airshed model.

Figure 3 shows the results of the Bergin study. The "CIT population" and "CIT spatial" labels refer to the urban airshed model results and correspond to ozone exposure measures or metrics that are based on population-weighted exposure or spatially-weighted exposures. The MIR legend refers to the values calculated using the more simplistic box model. The results shown have been normalized by dividing by the reactivity or exposure metric of a mixture of hydrocarbons that represent the composition of automobile exhaust. In this case the correlation between the reactivity values calculated for both the box model and the urban airshed models are very good, indicating that the reactivity values calculated with the simple box model adequately represent the

values calculated using a more realistic urban airshed model.

Another important factor that can contribute to the uncertainty of reactivity determinations is the chemical mechanism used to model the atmospheric reactions that result in ozone formation. The chemical mechanism may involve many tens of reaction steps, each defined by an individual rate constant. In the best circumstances, each rate constant has been experimentally measured and its associated experimental uncertainty is known. However, in many cases the rate constant is an estimate based on similar reactions or educated guesses. This adds more uncertainty to the chemical mechanism.

Several investigators have studied the uncertainties associated with the chemical mechanisms and the extent to which the uncertainties affect reactivity value determination. Yang et al. (1995) propagated the uncertainties in rate constants of the more important chemical reactions through a box model run and determined the uncertainties of the MIR value for 26 hydrocarbon species. The uncertainties (i.e., 1 standard deviation) ranged from 27% to 68%, even though the uncertainties of some of the rate parameters in the chemical mechanism were considerably higher (>100%). The analysis also showed that changes in rate parameters of many of the reactions correlated well with the changes in the MIR values of the 26 compounds. This indicates that the uncertainties in the relative reactivity values would be less than those calculated for the absolute reactivities. Bergin et al. (1997) looked at rate parameter uncertainty using the more sophisticated urban airshed model. They found that the relative reactivities are not very sensitive to reaction rate uncertainties. In summary it appears that uncertainty in reaction rates does not contribute too large an uncertainty to restrict the use of reactivity in regulations.

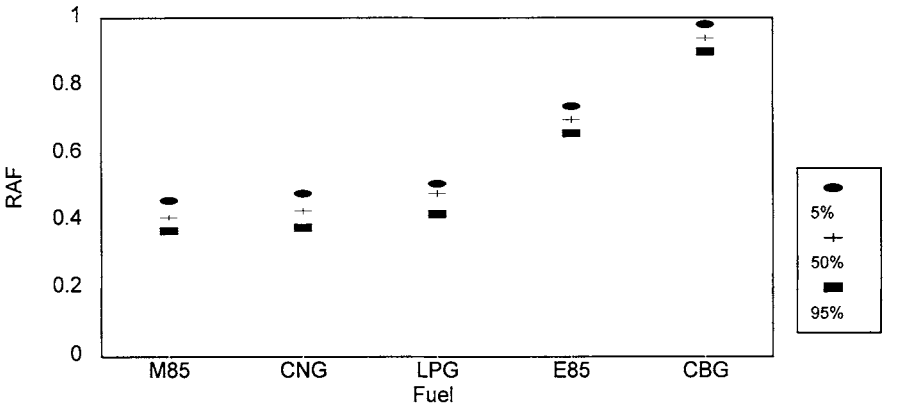

Figure 4. Variation in RAF's due to exhaust composition.

For the LEV/CF program, the reactivity values are used to compare exhaust emission reactivities of vehicles burning different types of fuels. Hydrocarbon species concentrations in exhaust emissions are inherently variable and the variability introduces uncertainty into determination of the RAF described earlier. The effect of the exhaust composition variability was studied by Yang et al. (1996) and showed that the additional uncertainty added by considering the exhaust variability was about 10%. An independent analysis (Russell et al. 1995) determined the effect of exhaust emission variability on the RAF for four alternative fuels and standard gasoline. The results displayed in Figure 4 show that the RAF's are relatively insensitive to the variability of the exhaust composition. The 5%, 50%, and 95% correspond to the 5th, mean, and 95th percentiles of each of the RAF values. The fact that the RAF's are ratios or represent relative reactivities contributes to the insensitivity and reinforces the use of relative or normalized values to minimize the uncertainty.

6. CONSUMER PRODUCTS

With the successful implementation of reactivity into the LEV/CF regulations, other

potential categories are now being investigated for incorporation of reactivity into their controls. This includes the consumer products category. Consumer products include many categories such as air fresheners, antiperspirants and deodorants, automotive windshield washer fluids, glass cleaners, hair sprays, floor polishes, and hair styling gels. Consumer products contribute about 15% of the total stationary source hydrocarbon emissions in California, or about 240 tonnes per day. To meet the requirements of California's air quality plan, consumer product hydrocarbon emissions are required to be reduced by 85% by 2010. To achieve this aggressive goal, hydrocarbon reactivity may be used as part of the strategy to "fine-tune" the 85% reduction goal.

As with the LEV/CF regulations, there are many challenges unique to the consumer products industry that need to be addressed before reactivity can adequately be incorporated into a regulation. Uncertainty, as with the LEV/CF regulations, is important. As described above, the RAF's developed for the LEV/CF regulation are defined as ratios of the reactivities of vehicle exhaust composed of similar hydrocarbon mixtures. Because of the similar hydrocarbon mixtures, the uncertainties of the different mixtures are somewhat correlated and by taking the ratio of the reactivities the uncertainties are reduced. Typical reformulations for some consumer product categories will involve changing relatively dissimilar (in that the uncertainties are not expected to be correlated) compounds and the magnitudes of the uncertainties associated with the formulations must be accounted for. For example, how will a regulation incorporate uncertainties to ensure that the reactivity of a new formulation is actually less than that of the old product? A trivial but realistic example would be reformulating a product using a hydrocarbon with a reactivity value of 4+/-1 with a new hydrocarbon with a reactivity value of 3+/-0.5. Does this switch actually reduce the reactivity of the product?

Another challenge for consumer products is that some of the consumer product hydrocarbons have not been studied as thoroughly as the hydrocarbon species found in auto exhaust. About 60% of the hydrocarbons in the consumer product inventory is comprised of ethanol, n-butane, isobutane, propane and isopropanol which have been well studied and their reactivity values are well known. Another 30% of the inventory is composed of petroleum distillates which contain alkanes, alkenes and aromatic compounds which also have better known reactivity values. However, the remaining 10%

of the hydrocarbons in the consumer products inventory have not been adequately studied, in part, due to lack of suitable analytical techniques for measuring these compounds. Therefore, reactivity value uncertainties are higher, and in some instances a useful reactivity value is not available. Resources must be directed toward studying these hydrocarbon species. Additionally, product formulation information may be proprietary, and the additional limitations this may bring about in developing and enforcing such a regulation need to be considered.

However, reactivity considerations (if the uncertainties are manageable) do offer the benefit of ensuring that less reactive compliant consumer products are realized. With existing mass based regulations requiring reduction of overall hydrocarbon mass in consumer products, there is a concern that more reactive hydrocarbon compounds will replace the existing compounds in products as they reduce their hydrocarbon content. In this instance, mass based regulations, operated in the absence of reactivity considerations, would potentially increase air pollution by increasing the overall reactivity of the complying product while reducing its mass of hydrocarbon compounds. Incorporation of reactivity in the regulation would prevent this scenario from occurring, and is an important reason to consider its use in the new regulations.

7. EXPERT ADVICE

Recognizing that there are many uncertainties associated with the use of hydrocarbon reactivity in regulations, the ARB formed two reactivity committees to assist in guiding its reactivity research activities and to provide expert advice on any hydrocarbon-reactivity-related topic. The Reactivity Research Advisory Committee (RRAC) is composed of several experts from the consumer products industry and provides a forum for informed dialogue between the industry and the Air Resources Board (ARB). The Committee's overall goals are to provide a forum for determining the reactivity research needs for the consumer products industry; to enhance reactivity research efforts by coordinating research activities (coordination would avoid duplication of studies and would provide opportunities for co-funding or augmentation of existing

and planned studies); to provide information relating to ARB and industry reactivity research activities; and to provide overall guidance on implementing hydrocarbon reactivity into consumer product regulations.

The Reactivity Scientific Advisory Committee (RSAC) is made up of independent respected scientists whose responsibility it is to make recommendations to the ARB on future reactivity-related issues at the request of the Board Chairman. Such recommendations will be advisory only, and will not be binding on the Board. The committee has considered topics such as what is the best reactivity scale to use, how should negligibly reactive compounds be defined, and how should compound trades and substitutions be implemented. Future meetings are planned to address reactivity concepts specific to the consumer product regulations being developed.

8. RESEARCH ACTIVITIES

Many aspects of hydrocarbon reactivity need further study to ensure that the use of the concept in regulations is appropriate. The ARB has supported research on hydrocarbon reactivity for several years as part of its overall program to study regional scale air quality problems. Current studies being funded by the ARB include determining the MIR values for compounds specific to consumer products. These compounds have typically not been studied for a variety of reasons but are now important because of the consumer product control strategies adopted by the ARB. Another study involves determining the uncertainty of calculated MIR's using a combination of mathematical techniques that will result in a more objective estimate of a hydrocarbon's reactivity value. Other studies are being conducted to improve hydrocarbon speciation profiles for aerosol paints, and to improve airshed models. Product studies are being conducted of poorly studied hydrocarbons. All of these research activities will ultimately lead to improved hydrocarbon reactivity estimates.

9. SUMMARY

The concept of reactivity has been and continues to be pursued by the ARB to provide more flexibility to industry to meet the increasingly stringent requirements that are necessary to maintain improvement of California's air quality. Hydrocarbon reactivity was successfully incorporated into the LEV/CF regulation by developing RAF's. The RAF's definition allows for reduction of many of the uncertainties associated with the hydrocarbon reactivity estimates. Other categories of compounds may not allow for similar reductions in uncertainties and it will be more difficult to use their reactivities in developing regulations with the current state of the science. This is the case with the consumer product regulations currently being developed. To aid the ARB in appropriately incorporating hydrocarbon reactivity into the regulatory process, expert panels have been formed and further research into reactivity is underway. The ongoing research and input from the expert panels will further the state of the science and ultimately will lead to more certain treatment of hydrocarbon reactivity.

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