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Project Summary

A Chamber and Modeling Study to Assess the Photochemistry of Formaldehyde

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A new analytical method for formaldehyde (HCHO) was implemented for use in the UNC outdoor smog chamber, and HCHO measurements obtained with this method were compared with those obtained using other analytical techniques. Six different calibration standards for HCHO were found to agree within ±2%, and the different HCHO analytical methods had precisions of ±10%. New experiments in which HCHO was an initial reactant and in which HCHO was produced chemically were performed. The older and newer HCHO analytical methods agreed to within 10% in these experiments.

A very explicit photochemical reaction mechanism for ethene and propene was formulated to explain the chamber observations. The ethene mechanism showed excellent agreement with chamber observations; the propene mechanism, however, did not perform as satisfactory. A comparison of these explicit mechanisms with the Carbon Bond IV (CB4) mechanism, which is used in several EPA air quality simulation models, showed excellent agreement for ozone (<10% error), nitrogen oxides, and hydrocarbon oxidation rates; the CB4, however, consistently underpredicted the HCHO maximum by about 13%.

An analysis of a simulation of an urban scenario showed that chemical production of HCHO was the dominant factor governing afternoon HCHO concentrations. Ethene and other olefins were the source of 58-62% of the HCHO produced and

aromatics were responsible for 10-12%.

It was concluded that the CB4 mechanism can be used to predict ambient HCHO levels with an error of about 20%.

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Introduction

Because of a growing concern about the health risks of exposure to formaldehyde, the U.S. EPA is considering regulating HCHO ambient levels. An initial exposure assessment conducted by EPA concluded that 80-90% of ambient HCHO is produced by the photochemical oxidation of hydrocarbon (HC) species. Thus, photochemical reaction models will have to be used to relate emissions and emissions controls to ambient levels of HCHO. Current photochemical models accepted by EPA for use in oxidant models were not specifically developed to predict HCHO. In fact, the model developers had reservations about the HCHO chamber data and, therefore, only made limited comparisons between predicted and observed HCHO. In particular, it had been suggested by model developers that the University of North Carolina (UNC) HCHO chamber measurements may have suffered from positive interferences and thus could be too high

by almost a factor of two. HCHO data obtained in a chamber facility operated by the Statewide Air Pollution Research Center (SAPRC) were lower (and thus more consistent with model predictions) than that from UNC, but the SAPRC data were more variable. Thus the accuracy of HCHO predictions obtained with existing photochemical models was uncertain mainly because of a lack of believable measurements of HCHO in the chamber data used to develop and test models.

The work described in this summary was carried out to determine if existing EPA photochemical reaction mechanisms can be used to predict accurate ambient levels of HCHO. The approach taken was to a) implement and test newer and more reliable HCHO analytical methods and calibration sources in the UNC chamber, b) conduct new chamber experiments with the newer and older HCHO analytical methodology, c) compare new results with those in the existing 12-year data base used to develop the EPA models, d) perform modeling exercises to diagnose problems in data and model formulations, and e) examine HCHO predictions in light of the new information.

Formaldehyde Measurements

A new diffusion-scrubber, fluorescence detector HCHO monitor (Dasgupta Monitor) was implemented and its performance was compared to seven other techniques for measuring HCHO. Several conclusions were drawn from this work:

- All formaldehyde sources used as calibration standards agreed to within ± 2%.
- The paraformaldehyde permeation tube was shown to be a very accurate and stable calibration standard for HCHO.
- Significant interferences did not appear in any test of either the CEA 555 HCHO monitor (in use for 11 years at UNC) or the Dasgupta HCHO instrument (in use for 3 years at UNC).
- There is weak evidence that the CEA response, when not zero-checked for twenty minutes every three hours, may exhibit a positive drift; data collected during such periods may not be correctable. When zero-checked regularly, the CEA response does not show any significant bias.
- There is no evidence that the Dasgupta HCHO instrument exhibits more than a 5% bias at any time. Several aspects of this particular wet-chemical fluorescence technique, however, can make some individual data

points more uncertain than others. When the Dasgupta HCHO instrument is operated in a well-maintained mode, it exhibits a precision of ~6 ppb at a level of ~155 ppb (3.8%).
- Despite concerted and on-going efforts at QA and calibration, uncertainty persists regarding some of the HCHO data taken over the past 12 years in the UNC chambers. Errors in recording and processing the data are always possible, and calibration standards have not always been as available and reliable as they are today. Thus, there are some HCHO data in the UNC chamber database that cannot be shown to be wrong, but which are contrary to expectations given our current understanding of HCHO chemistry.
- Based upon the comparison of the Dasgupta monitor with the chromotropic acid bubbler method and the FTIR method used at SAPRC, it appears that the HCHO standards used at SAPRC are accurate and consistent with the UNC and EPA standards to ± 2%.
- The SAPRC chromotropic acid bubbler method appears to be erratic at high, reasonably steady levels of HCHO. It also can have a low bias for all measurements taken on a given day, even if it had no bias the day before. The bubbler method also never measured higher than the Dasgupta method in seven experiments.
- The newer and older instruments showed excellent agreement for a wide range of chamber HCHO levels. Thus we have strong evidence that the UNC HCHO chamber data are accurate. Therefore, any disagreement between model and chamber observations is probably due to inaccurate representations in the models.

Explicit Photochemical Mechanism

An explicit photochemical reaction mechanism was formulated using existing kinetics data reviews and the literature. The mechanism includes explicit chemistry for methane, formaldehyde, ethane, acetaldehyde, organic nitrates and peroxyacetylnitrate, ethene, glycoaldehyde, glyoxal, propene, and detailed radical representations. Particular attention was paid to the state of knowledge for the fate of the Criegee biradicals as review suggested that this was the most ill-defined aspect of olefin chemistry in

the existing EPA mechanisms. The explicit mechanism was used to simulate a) ozone-ethene kinetics experiments conducted by several investigators, b) nighttime ozone-ethene and ozone-propene experiments conducted in the UNC chamber, and c) sunlight irradiated experiments containing oxides of nitrogen (NO_x) and CO, HCHO, acetaldehyde, ethene, or propene that were also conducted in the UNC chamber. In almost all cases except propene, the agreement between the simulations and the observations was excellent for NO_x, O_3, HCs, and HCHO. For propene, the theory and the sparse kinetics information for the two-carbon Criegee biradical were in substantial disagreement with the chamber results for NO_x-propene experiments. Some modelers made ad hoc adjustments to the propene-ozone mechanism to allow better simulation of chamber data and in doing so may have compromised HCHO predictions. Several conclusions were reached based on the simulation tests:
- Our chamber simulations support the higher absorption cross-sections of Moortgat compared to Bass.
- We present indirect and nonconclusive evidence that hydroxy-ethyl nitrate is formed through reaction of NO with the ethene-OH adduct to an extent of 4%.
- The yields given in the literature for stabilized Criegee biradicals for O_3 + olefin reactions are based on the loss of either O_3 or the olefin, both of which have other consumption pathways in the experimental system. Therefore, when these yields are used in a mechanism, they should be corrected to reflect these other losses.
- The reactions of the C_1 Criegee biradical appear to be reasonably well understood, with the exception of its reaction with water. We presented indirect and inconclusive evidence that a large fraction of the reaction of this biradical with water could lead to HCHO and H_2O_2. If our assumed pathway is correct, there exists a large potential for forming H_2O_2 by dark reactions.
- The chemistry of glycoaldehyde may be sufficiently different from that of acetaldehyde that the CB4 approximation of representing glycoaldehyde as acetaldehyde is questionable.
- New chamber experiments using glycoaldehyde as the primary reactant are needed for continued model testing. Chamber experiments employing glyoxal as the primary reactant would also be beneficial.

- A technique for the reliable, real-time measurement of formic acid in ethene-NO_x chamber experiments should be developed.
- More high concentration ethene-NO_x chamber experiments should be conducted on cool days to investigate the anomalously high HCHO formation observed in the cool-weather experiments carried out in this study.
- Although the model fits to the very wide range of experiments simulated here were excellent, we believe that further work is needed on the UNC chamber wall model.
- The excellent "goodness-of-fit" of the explicit ethene mechanism to a large range of conditions in the UNC chamber over a 12-year period is strong evidence that the mechanism does explain the observed chemistry in a manner consistent with known kinetics data. Although there remain some doubtful elements in the ethene mechanism, it is at present the best explanation we can construct, and we believe that it can be taken as a standard against which to measure the performance of the ethene portion of air quality simulation mechanisms in common use by EPA.

Performance of the CB4 Mechanism

The Carbon Bond Four mechanism was used to simulate several ethene and propene chamber experiments and the results were compared to those obtained with the explicit mechanism. These tests of CB4 used a) HCHO photolysis rates derived from the cross-sections reported by Moortgat, b) the newest UNC chamber characterization model, and c) the latest information on in-chamber actinic fluxes. The conclusions reached from analyzing these simulations were:
- With regard to predicting O_3, the CB4 mechanism is excellent for ethene-NO_x experiments. It is slightly worse than the explicit mechanism for NO and NO_x, but not significantly so.
- At all levels of ethene tested, the CB4 consistently underpredicted the HCHO maxima observed in ethene-NO_x experiments by about 13%. The cause of this underprediction is complex and related to a number of approximations used in the CB4:
  a) There are too few radical-radical termination reactions in the CB4 for it to simulate the correct efficiency of HO_2 production from the ethene + OH reaction; it therefore predicts too much ethene consumption and too

much production of HO_2 and NO_2.
  b) Acetaldehyde is not a good substitute for glycoaldehyde in these high concentration experiments.
  c) Certain important pathways in the Criegee biradical reactions have been omitted in the CB4.
- Like the explicit propene mechanism described in this work, the CB4 mechanism does poorly in simulation propene-NO_x experiments with initial propene concentrations above ~1.5 ppmC.
- Previous testing of the CB4 with toluene and xylene experiments from the UNC chamber showed that the CB4 overpredicts HCHO. Confirming toluene and xylene experiments were conducted in this study and these experiments show levels of HCHO similar to those obtained in the previous experiments. Thus, we conclude that the CB4 mechanism overpredicts HCHO yields from toluene and xylene by about a factor of two. The observed yields of HCHO are low, however, amounting to only about 3% of the aromatic carbon.

Urban Simulations

A time-resolved mass balance method was used to analyze predictions of HCHO obtained in a simulation of a typical urban scenario. This analysis showed that:
- Chemical production of HCHO accounts for 70-90% of the total HCHO observed. A "pseudo-photostationary state" is reached at approximately the same level regardless of whether or not initial HCHO and HCHO emissions are included in the simulation.
- Large early morning dilution rapidly reduces any HCHO initially present and most of the initial HCHO is gone by 1300 LDT (maximum O_3 occurred at 1900 LDT).
- Over the day, the olefins and acetaldehyde were responsible for approximately 60% of the HCHO that was produced. The non-ethene olefins made their contribution in the morning, ethylene contributed all day, and acetaldehyde increased its contribution to HCHO production near the end of the day.
- An analysis of the CB4 mechanism and the UNC chamber data suggests that the CB4 is able to predict HCHO formation in urban HC mixtures fairly accurately. It appears, however, that the CB4 underpredicts HCHO formation from olefinic HCs and overpredicts HCHO formation from

aromatic HCs. Thus, the good agreement appears to be due to compensating errors.

Conclusions

The purpose of this study was to determine if present photochemical reaction mechanisms can be used to predict accurate ambient levels of HCHO for various scenarios of HC and NO_x. We believe that this is probably the case for the most commonly used EPA mechanism, the Carbon Bond Four mechanism (CB4). Some parts of the CB4 (and other similar mechanism), however, are not fully accurate descriptions of the important HCHO producing chemistry. The errors are probably small, only resulting in approximately a 20% error in maximum HCHO predictions. The magnitude of the error depends upon the composition of the HC mixture used in the simulation because there are compensating errors in different HC classes. A second weakness that CB4 has for this application is that it has a very compressed representation for the most important species producing HCHO, the various olefin classes. For example, acetaldehyde is used in the CB4 to represent internal olefins. The accuracy of the CB4 for predicting HCHO formation could be improved by slightly expanding the representation of olefins in the mechanism.

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