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Project Summary

An Experimental and Modeling Study of the Photochemical Reactivity of Heatset Printing Oils

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A series of environmental chamber experiments and computer model simulations were carried out to assess the atmospheric ozone formation potential of the respresentative heatset printing oils Magie-47 and Magie-470 relative to that of ethane. n-Pentadecane, a representative major constituent of these oils, was also studied. The results showed that n-pentadecane and the printing oils tend to slow down the initial rate of ozone formation in NO_x-air irradiations, but they also caused higher final ozone yields in some surrogate-NO_x-air experiments.

The results of these experiments were used to test current models for the reactivities of ethane and n-pentadecane. The model predictions fit the results of most of the experiments within the experimental uncertainty, though some discrepancies were observed. It is unclear whether the discrepancies are due to problems with the mechanism or to experimental difficulties.

The model was used to estimate the reactivities of ethane and n-pentadecane for several idealized model scenarios representing urban air pollution episodes. The predicted atmospheric reactivities of n-pentadecane and the printing oils relative to ethane were found to be highly dependent on the conditions of the model scenario. Thus, decisions on whether regulation of emissions of printing oils is beneficial in reducing atmospheric ozone must take into account the range of conditions of the airsheds into which they are emitted.

This Project Summary was developed by EPA's Atmospheric Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Web-offset printing operations can result in the emission of printing oils into the atmosphere, and these vaporized oils may undergo photochemical reaction which contribute to the formation of atmospheric ozone. Since ozone is a major air quality problem in many urban areas, the precursors to ozone formation are subject to regulatory control under State implementation plans. To determine whether controls of printing oil emissions need to be included in such plans, it is necessary to establish whether the presence of these oils in the atmosphere can contribute significantly to ozone formation, i.e., to establish whether these oils can be considered to be "reactive" relative to ozone formation.

To be considered to be "reactive," an organic compound or mixture must (1) be sufficiently volatile so that it can react in the gas phase, (2) react in the atmosphere sufficiently rapidly that its reactions can be of significance, and (3) react in such a manner that it contributes to ozone formation. In many cases it is obvious whether or not a compound or mixture can be considered to be reactive or unreactive. If a compound has a negligible volatility or is essentially inert in the atmosphere, it can be considered

to be unreactive. If, however, relatively low concentrations of a compound cause significant ozone formation when irradiated in the presence of NO_x in environmental chambers, then it is clearly reactive. In cases when a compound or mixture is either marginally volatile, reacts in the atmosphere but does so relatively slowly, or reacts in such a way that it is not clear whether or not its reactions enhance or suppress ozone formation, then it is not immediately obvious whether to classify this compound or mixture as reactive or unreactive. In these cases, the current regulatory policy is to use the reactivity of ethane to define the borderline between reactive and unreactive organic compounds.

To obtain the data necessary to assess whether heatset printing oils must be considered to be reactive, Battelle, Columbus, Laboratories had previously studied volatility of representative printing oils and their photochemical reactivity in environmental chamber irradiations. The results of their study indicated that the printing oils cannot be considered to be unreactive on the basis or volatility, but the results of the environmental chamber experiments were ambiguous with regard to whether they react in a manner which promotes ozone formation. Some of the experiments indicate that the printing oils studied are somewhat more reactive than ethane, while others indicated that they were less reactive. A significant amount of this uncertainty is due to problems in interpreting environmental chamber data when used to study relatively unreactive compounds, and because the conditions of environmental chamber experients are never exactly the same as those in the ambient atmosphere. Previous studies indicated that these differences become highly significant when comparing relatively unreactive substances such as ethane and printing oils.

In principle, computer model simulations, where the chemical mechanisms used in the model is tested by comparing its predictions against the available environmental chamber data, can be employed to predict reactivities under atmospheric conditions. In this way the computer model is used as a means of correcting for chamber effects and making extrapolations from conditions of environmental chamber experiments to those in urban airshed. However, for this procedure to be appropriate as a basis for control decisions, it is necessary that the model employed be consistent with our current understanding of atmospheric chemistry and the atmospheric reactions of the major constituents of the printing oils, which consist primarily of saturated hydrocarbons with an average molecular weight corresponding to that of n-pentadecane (n-$C_{15}H_{32}$).

High molecular weight alkanes are expected to be reactive in the sense that they have relatively high rate constants for reaction with hydroxyl radicals (the primary mode of reaction of saturated compounds in the atmosphere), but they also react in a manner which removes radicals and NO_x from the system. This latter characteristic tends to reduce their reactivity, and may even make them ozone inhibitors under some conditions. Computer model simulations could indicate whether this is so under atmospheric conditions, provided the mechanism is adequately characterized and tested. However, the available chamber data were not sufficient to establish the reliability of computer models for the purpose of predicting the reactivities of high molecular weight alkanes under atmospheric conditions.

Because of this need for further studies concerning the atmospheric reactivity of the printing oils, the EPA contracted to the Statewide Air Pollution Research Center (SAPRC) of the University of California at Riverside to carry out additional environmental chamber experiments to provide additional data needed for model testing, and to use these data as a basis for evaluating their atmospheric reactivities. This Project Summary summarizes the results of that study.

Experimental

The experiments were carried out in the SAPRC 6400-liter indoor Teflon chamber (ITC), which uses blacklamps as the light source. The experiments consisted of NO_x-air irradiations of the representative printing oils Magie-47 and Magie-470, of ethane, and of the representative printing oil constituent n-pentadecane, both by themselves (with trace amounts of propene present in order to test the effects of their reactions on radical levels), and when added to a standard "mini-surrogate"-NO_x-air mixture. This "mini-surrogate" consisted of four hydrocarbons (n-butane, propene, *trans*-2-butene, and m-xylene) designed to be a simplified representative of the mixture of organics emitted into polluted urban areas. The experiments also included an appropriate array of control and characterization runs necessary for the data to be sufficiently well characterized for model testing. A total of 33 environmental chamber irradiations were carried out, and detailed tabulations of the data obtained are available from the author in computer readable format.

Computer Model Calculations

Computer model simulations were carried out as part of this study to determine whether our current understanding or estimates of the atmospheric reactions of n-pentadecane (the representative printing oil constituent), and of ethane are consistent with our experimental results, and to estimate the relative reactivities of these compounds under conditions of idealized ambient pollution scenarios. The chemical mechanism used for the NO_x-air reactions of ethane and the surrogate components was that recently developed and tested by us under USEPA funding. That mechanism did not include the reactions of n-pentadecane, and these had to be estimated as part of this study.

Although prior to this experimental study there have been no data available concerning the atmospheric reactions of n-pentadecane, estimates can be made based on extrapolating our knowledge of the atmospheric reactions of lower alkanes. However, there is a major uncertainty concerning the overall organic nitrate yield in the n-pentadecane reactions, and two alternative mechanisms, designated model "A" and model "B", were employed in an attempt to bracket the range of uncertainty. Model "A" is based on assuming relatively high nitrate yields consistent with theoretical estimates, and model "B" is based on assuming lower nitrate yields suggested by our previous modeling of C_6-C_8 n-alkane-NO_x-air experiments.

Results

One run each was carried out in which ethane, n-pentadecane, Magie-47, or Magie-470 were irradiated in NO_x-air mixtures without other added reactants besides propene and n-butane tracers (10 ppb each) added to monitor radical levels. In all cases the addition of the test substance tended to suppress radical levels, but the suppression of radical levels was significantly greater for

n-pentadecane and the printing oils than it was for ethane. In particular, n-pentadecane, Magie-47, and Magie-470 suppressed radicals by factors of ~50, ~40, and ~25 more than ethane, respectively. The model simulations fit the ethane runs to within the range of uncertainty caused by the variability of the chamber radical source. The experimental results of the n-pentadecane run fell somewhat between the predictions of the two n-pentadecane mechanisms (models "A" and "B"), while the results of the Magie-47 run were well simulated by the more reactive model "B", and both models underpredicted the reactivity observed in the run with Magie-470.

Most of the experiments consisted of runs where either ethane, n-pentadecane or one of the printing oils were added to a standard "mini-surrogate"-NO_x mixture, and of control runs where the standard surrogate-NO_x mixture was irradiated with no test compound added. The results of these experiments were analyzed to determine the "incremental reactivities" of the test compounds, defined as the change (in ppm) in the 1-, 2-, 3-, or 6-hour ozone yields caused by the addition of a test compound to the standard surrogate-NO_x mixture, divided by the ppmC of the test compound added. The incremental reactivities of ethane in these experiments were found to be 2 to 5 ppb ozone per ppmC ethane added, in good agreement with model predictions. The incremental reactivities of n-pentadecane and the printing oils are shown, as a function of amount of compound added and irradiation time, in Figure 1, where they can be compared with predictions using the two n-pentadecane mechanisms.

It can be seen that under some conditions the addition of n-pentadecane or the printing oils inhibit ozone, and in others they enhance it, with the effect depending significantly on both reaction time and the amount of test compound added. The predictions of the models agree qualitatively with the experimentally determined incremental reactivities, with the more reactive n-pentadecane model "B" being more consistent with most results, though there are discrepancies. However, given our current limited knowledge of the details of the atmospheric photooxidation reactions of the higher alkanes and the products formed, and the experimental difficulties in obtaining precise measures of reactivity for relatively unreactive compounds, the performance of the model in simulating these results is probably as good as can reasonably be expected at the present time.

To provide an indication of the model predictions of the relative reactivities of ethane and the printing oils (as represented by the two n-pentadecane mechanisms) for conditions more representative of polluted urban atmospheres than can be attained with environmental chamber experiments, model simulations of incremental reactivities were carried out using several idealized airshed model scenarios. The specific quantities calculated were the "limiting incremental reactivities," defined as the difference in the maximum $\Delta([O_3]-[NO])$ in the simulations with and without the added test compound, divided by the amount (on a mole carbon basis) of test organic added, at the limit as the amount of test compound that goes to zero. The airshed scenarios were based on three different model formulations of emission schedules, transport, dilution, and back-

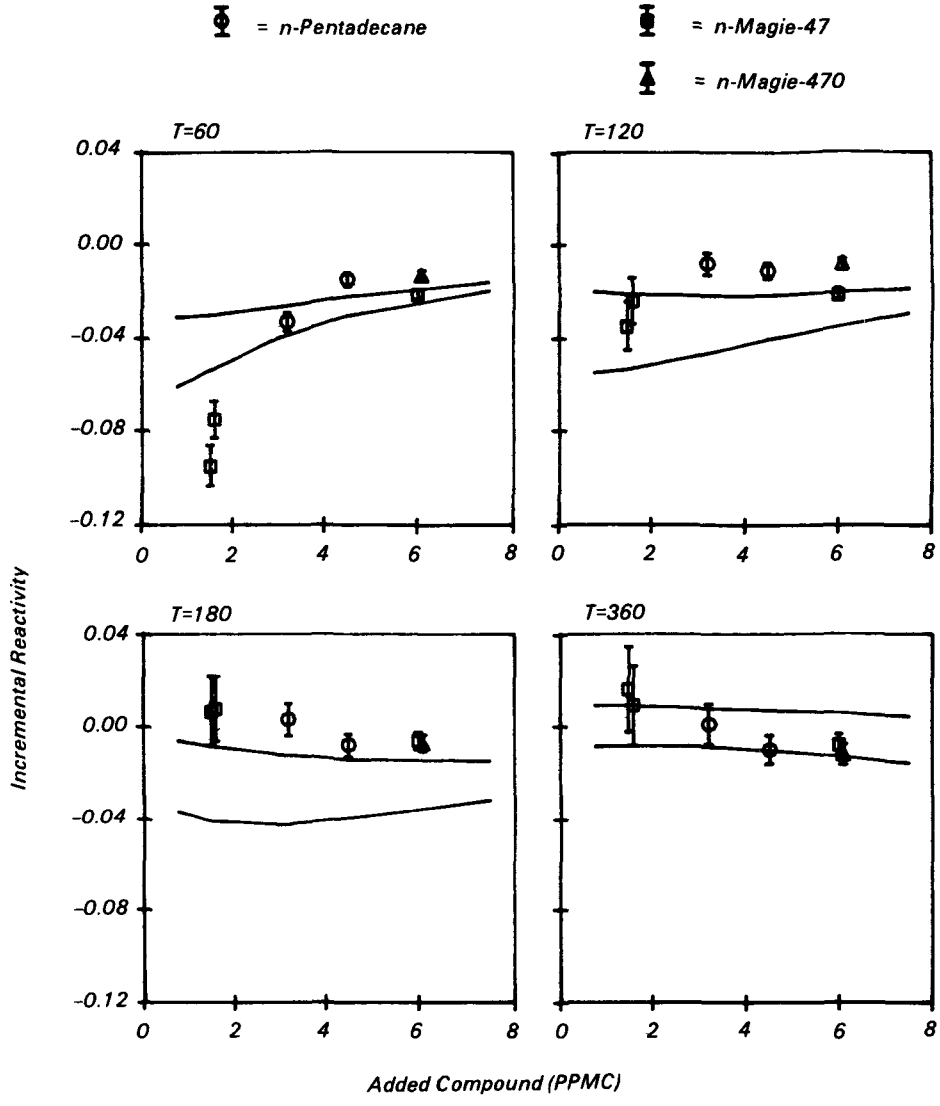

Figure 1. Plots of experimental and calculated incremental reactivities of n-pentadecane and the printing oils Magie-47 and Magie-470 against amounts of test substance added in the ITC "mini-surrogate"-NO_x-air experiments. O = Experimental. (See above for symbols for different types of runs.) ——— = Model calculations of incremental reactivities for the times shown. The lower lines were calculated using n-pentadecane Model A, and the upper lines were calculated using Model B.

ground conditions, with the "EKMA-1" and "EKMA-3" scenarios being based on city-specific EKMA defaults for low and high dilution conditions, respectively, and the "MD" scenario being an idealized representation of a multi-day pollution episode in the California South Coast Air Basin. Two different surrogate mixtures, "Surg-4", and "Surg-8", which differ in complexity but are similar in overall reactivity, were employed to represent base case ROG emissions in these scenarios. For comparison purposes, reactivities were also calculated for the conditions of our indoor Teflon chamber (ITC) experiments. For each scenario, incremental reactivities were calculated for a range of ROG/NO_x ratios.

The calculated reactivities of ethane were found to be always positive, and to depend primarily on the amount of dilution occurring in the scenario, being highest in the highest dilution "EKMA-3" scenario, and the lowest in the no-dilution "ITC" scenario. The reactivity of ethane also depends on the ROG/NO_x ratio, being the highest for ratios slightly less than those most favorable for ozone formation. The maximum reactivity of ethane was calculated to be somewhat higher when the Surg-8 mixture is used for the base case ROG surrogate, and was also calcualted to increase with the number of days in the multi-day simulation.

The calculated reactivities for n-pentadecane were found to be much more variable and dependent on the conditions of the scenario than was the case with ethane. Regardless of which of the two n-pentadecane mechanisms was employed, n-pentadecane was predicted to inhibit ozone under some conditions, and to be somewhat more reactive than ethane under others. This is shown in Table 1, which gives the ratios of the reactivities calculated for the two n-pentadecane mechanisms, relative to those calculated for ethane, for the conditions of the various scenarios. It can be seen that the calculated reactivities of n-pentadecane relative to ethane are highly dependent on the ROG/NO_x ratio, the n-pentadecane mechanism assumed, and the nature of the scenario and the base case ROG mixture, in approximately that order of importantce. The relative reactivities are the highest under the conditions most favorable to ozone formation, tending to become negative both at low and at high ROG/NO_x ratios, due respectively to the radical termination and the NO_x removal characteristics of the n-pentadecane photooxidation mechanism.

Table 1. *Ratios of Calculated Incremental Reactivities for n-Pentadecane to Those for Ethane for the Airshed and ITC Scenarios*

	n-Pentadecane Reactivity/Ethane Reactivity					
	ITC	*EKMA-1*		*EKMA-3*	*MD, Surg-8*	
ROG/NO_x	*Surg-4*	*Surg-4*	*Surg-8*	*Surg-8*	*Day 1*	*Day 2*
n-Pentadecane Model "A"						
4	*-12.6*	*-6.4*	*-0.7*	*0.8*	*-1.0*	*0.5*
8	*-10.8*	*-4.0*	*0.5*	*1.2*	*-0.8*	*1.2*
12	*-8.3*	*-2.7*	*-0.5*	*0.0*	*0.3*	*0.9*
16	*-7.3*	*-4.5*	*-2.5*	*-1.6*	*-0.7*	*-0.2*
40	*-2.8*	*-14.1*	*-13.3*	*-10.4*	*-11.4*	*-9.3*
n-Pentadecane Model "B"						
4	*-4.9*	*-1.5*	*1.7*	*2.1*	*1.6*	*2.3*
8	*-3.3*	*-0.1*	*2.2*	*2.2*	*1.3*	*2.2*
12	*-1.3*	*0.9*	*1.7*	*1.6*	*1.9*	*2.0*
16	*-0.2*	*-0.1*	*0.8*	*0.8*	*1.6*	*1.6*
40	*2.6*	*-5.2*	*-4.8*	*-3.8*	*-3.8*	*-3.2*

Conclusions

The currently available experimental data and theoretical estimates and calculations suggest that, with respect to atmospheric ozone formation, it is more probable than not that under some conditions the printing oils are more reactive than ethane. On the other hand, it is also clear that under other conditions the printing oils will inhibit ozone formation. Although in theory airshed model calculations could be used to estimate the reactivities of the printing oils for specific airsheds, the extreme sensitivity of the predicted reactivities to the conditions of the airshed into which they are emitted, combined with the uncertainties in the photooxidation mechanisms for their major constituents, makes such estimates subject to considerable uncertainty. Until more is known about the details of the atmospehric photooxidation mechanisms of the higher alkanes and other components of the printing oils, and how their reactivities depend on the conditions of the airsheds where they are emitted, it will not be possible to make definitive conclusions as to whether the printing oils should be judged to be reactive for regulatory purposes.

Finally, it should be recognized that this study addressed only the effects of emissions of the printing oils on ozone formation. The emissions of these oils could have other impacts on air quality, such as aerosol formation, formation of toxic products, etc., which should also be taken into account in making any decisions on whether to regulate the emissions of these oils. A discussion of these aspects is beyond the scope of this study, but obviously they should not be ignored.

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The complete report, entitled "An Experimental and Modeling Study of the Photochemical Reactivity of Heatset Printing Oils," (Order No. PB 88-113 253/AS; Cost: $19.95, subject to change) will be available only from:
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