

Particle Production by Polymer Pyrolysis: Mass-Spectrometric Investigation

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Synopsis

Mass-spectrometric techniques were applied to elucidate the mechanism by which polymers release condensation nuclei during pyrolysis.

INTRODUCTION

Van Luik and Ripperre reported the effect of various gases on the production of condensation nuclei from warm polymers.¹ Walther investigated this effect as a possible method of analyzing for trace gases in the atmosphere.^{2,3} Trace gas analyses are difficult because of low concentrations, interferences, and collection inefficiencies; a simple field method for the determination of carbon monoxide in the atmosphere would be desirable. Walther investigated the effect of various gases on the production by polymers of condensation aerosols upon being heated, measuring the aerosol with a condensation nuclei meter. He reported² that most trace gases in N₂ or O₂-N₂ mixtures enhance the aerosol production but that CO depresses aerosol production. Subsequently, we investigated the effect of CO on the production of condensation nuclei from a number of warm polymers of widely differing molecular architecture, with the view of developing a new analytical method.^{4,5}

We used an experimental apparatus consisting of a gas source, a tube containing Ag₂O, a flowmeter, a bubbler to humidify the gas stream, a converter in which the gas stream reacted with the polymer, a nucleus counter and recorder, and the requisite valves, heater, stirrer, etc. The gas source was either room air passed through a Gelman Type E glass filter or filtered tank air having a dew point of -58°C and containing 105 ppm CO. The room air humidity varied from 20% to 40% (dew points from -2° to +8°C), but it was usually near the midpoint of the range. Either gas flow could be diverted through a glass frit bubbler containing ultra-filtered and deionized water which we believe saturated the gas stream at 20°C. The converter was a 250-ml beaker fitted with a plug carrying inlet

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and outlet tubes, all of stainless steel. The plug was sealed into the beaker by a three-legged brass spider screwed to a brass clamping ring below the beaker flare. The temperature of the converter was held to within 0.2°C.

The General Electric continuous-condensation nucleus counter was operated at approximately 23 cm (9 in.) Hg vacuum. A glass-Teflon needle valve in the line controlled the flow and maintained it at about 5.5 l./min as the various three-way valves were manipulated. The pressure drop across the tube containing Ag₂O was the greatest and therefore was the limiting factor on setting the flow level.

The upper operating temperature limit was set by the silicone oil bath, which began to smoke above 215°C. Smoke could interfere with accuracy of the nucleus count, despite the two glass fiber filters in the flow train.

Polymers investigated ranged from a straight hydrocarbon oil through waxes, esters, and aromatics to a silicone.

We found that water vapor invariably enhanced aerosol production and that CO invariably depressed aerosol formation. Water vapor and CO in combination gave variable results, not correlatable with polymer molecular architecture. We further reported that the magnitude of the changes in all cases depended on the level of the thermally produced aerosol which makes it impractical to use this phenomenon in its present stage of development as a field method for analyzing for CO in ambient air.

Walther, following Madorsky⁶ had theorized that the reactive gas molecules attack weak links in the polymer chains, producing successive scissioning of the chain leading to molecular fragments short enough and volatile enough to escape from the bulk polymer and aggregate to form the detected condensation nuclei. The depressant effect of CO was explained by its ability, alone of all the gases tested, to bind up broken polymer linkages with its carbonyl form.

Although the effect of trace gases on the production of condensation nuclei from warm polymers has been adequately demonstrated, it is not much better understood in 1972 than it was in 1962. Particularly, the mechanism of nuclei production and the knowledge of the reaction products were unknown. The present study attempted to gain this knowledge as a means of elucidating the effect. Reaction products were collected in a freeze-out trap and analyzed by mass spectrometry.

EXPERIMENTAL

Equipment

The apparatus used previously by Fischer and Lodge^{4,5} was used again, but with the first filter and the first glass-Teflon three-way valve interchanged (see Fig. 1) so that both the tank gases and room air passed through the filter before entering the converter. Glass U-traps with vacuum stopcocks were connected to the glass-Teflon sampling valves and immersed in an isopropanol-dry ice slush at -85°C to collect the reaction products.

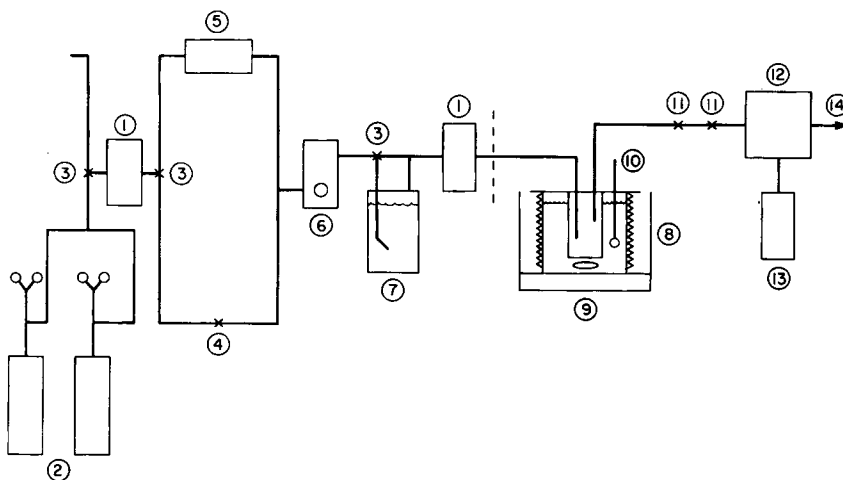


Fig. 1. Schematic of gas flow train: (1) Gelman Type E glass fiber filter; (2) gas cylinders; (3) glass-Teflon three way valve; (4) glass-Teflon needle valve; (5) tube containing Ag_2O ; (6) 10 lpm flowmeter; (7) glass frit humidifier; (8) stainless steel converter in insulated and air-lagged silicone oil bath; (9) temperature-controlled hot-plate magnetic stirrer; (10) thermometer; (11) glass-Teflon sampling valve; (12) GE continuous-condensation nucleus counter with pump; (13) recorder; (14) to laboratory duct system. N.B., System to right of vertical dashed line is stainless steel, except for two valves which are 15 cm of glass and 4 cm of Teflon.

The mass spectrometer is a CEC 21-103 model with modifications by David C. Sheesley and Roger C. Neuscheler of NCAR to improve the stability of the magnet and high-voltage system, to provide a more elaborate heated-inlet system, and to provide desorption traps ahead of the inlet system.

Polymers

A straight hydrocarbon oil, Apiezon C (Biddle) and polystyrene (Dow) were selected from those polymers previously used since they were well behaved in their pyrolysis.

Gases

Argon and argon-containing 10 ppm CO were used as the test gases. Conforming to our previous method of reporting data as an E/C ratio, where C is the concentration of condensation nuclei produced thermally in filtered room air and E is the concentration in the presence of the experimental variable, the results in Table I were obtained. The room-temperature results indicate that the tank gases themselves contain condensation nuclei. The results, after passage through the filter, which reduces the nuclei count from about $7000/\text{cm}^3$ in room air to the filtered-air background of about $100/\text{cm}^3$, indicate that the nuclei are either very small or gaseous.

In the presence of a warm polymer, the effect of the contaminating nuclei is not so pronounced, but it still exists to the point that the previously re-

ported nuclei-depressant effect of CO (E/C less than unity)^{4,5} is not apparent. The Ar-CO is cleaner than the Ar so that the lower E/C in the presence of the polymer is not due to the CO depressant effect alone. However, the CO depressant effect is probably still operative since a change back to filtered room air brings the count back to the C value directly from Ar but a change from Ar-CO lowers the count below C for a few minutes, then returns it to C .

The mass spectrometer indicated that the Ar tank gas contained H₂O, CO, CO₂, and traces of NH₃ and N₂O, and that the Ar-CO tank gas contained H₂O and CO₂. No consistent organic contaminants were found in either tank. Filtered room air was found to contain H₂O, CO, traces of NH₃, N₂O, and formaldehyde.

Method

The polymers were dissolved in a solvent and placed in the converter beaker, and the solvent was evaporated to leave a film of polymer approximately 100–150 μm thick.

The converter was brought up to the working temperature with filtered room air; the appropriate tank gas was then introduced, if desired, and the nuclei count observed. The cold U-trap was connected to the line, and the reaction products were collected for about 2 hr with periodic interruptions to check the nuclei count. Table II itemizes the operations.

It was intended to incorporate water vapor into the reaction scheme as was done previously.^{4,5} However, the small amount of water normally present in room air caused trouble by plugging the sampling trap and "drowning out" the mass spectrometer through rapid adsorption and slow desorption within the instrument. The latter interfered with the detection of subsequent peaks. Accordingly, water vapor was not deliberately added to the system.

The pyrolysis runs were made at higher temperatures and nuclei counts than usual in order to increase the amount of material available for analysis.

The sample in the dry-ice bath was transferred to the mass spectrometer for analysis involving carrying out scans to the C₂₀ m/e region of 280. Nothing significant over 100 was found. The sample was held at -85°C while the head gas was cryogenically pumped to a -180°C holding trap. After the sample was isolated, the holding trap was heated and pumped on to introduce the sample into the mass spectrometer. The procedure was repeated with mechanical rather than cryogenic pumping, and with the traps at temperatures of -85°C , 0°C , about 22°C , 100°C , and finally as high as 300°C . At each combination of trap temperatures, mass spectrometer scans were made. The recorder strip charts were manually digitized and the m/e peak numbers and peak heights were put onto punch cards.

The data were processed with a CDC 6600 computer program modified by Roger C. Neuscheler of NCAR from one developed by Tunncliffe and Wadsworth.⁷ The program contains a library of ASTM mass spectra designed

for the operating conditions of the NCAR mass spectrometer. The library is on magnetic tape in the form of an ordered matrix of m/e peaks for use in a mass-discriminating subprogram and a list of the compounds that furnished the peaks. The subprogram takes as input the sample mass spectrum and the physical conditions under which it was obtained. After calculating a sample matrix, the sample and library matrices are compared, beginning with the peak of highest amplitude, to select the compounds in the library that could have given the sample peaks. Least-squares regression analyses are applied until the residual is insignificant. The output is a listing of the calculated and input sample spectra and a listing of the compounds found.

The mass spectra included in the computer program library are:

Nitrogen	<i>cis</i> -2-Butene
Oxygen	<i>trans</i> -2-Butene
Neon	Propadiene
Argon	1,2-Butadiene
Water	1,3-Butadiene
Hydrogen sulfide	Acetylene
Hydrogen chloride	2-Methylpropene
Carbon monoxide	2-Methyl-1-butene
Carbon dioxide	Benzene
Ammonia	Toluene
Nitrous oxide	<i>o</i> -Xylene
Sulfur dioxide	<i>m</i> -Xylene
Trichloromethane	<i>p</i> -Xylene
Methane	Ethanol
Ethane	<i>n</i> -Propanol
Propane	Isopropanol
<i>n</i> -Butane	<i>n</i> -Butanol
<i>n</i> -Pentane	Formaldehyde
<i>n</i> -Hexane	Acetaldehyde
<i>n</i> -Octane	Propionaldehyde
2-Methylpropane	Acetone
2-Methylbutane	Butanone
2-Methylpentane	Ethylamine
3-Methylpentane	<i>n</i> -Propylamine
2,2-Dimethylpropane	<i>n</i> -Butylamine
2,2-Dimethylpentane	Trimethylamine
2,3-Dimethylpentane	Diethylamine
2,4-Dimethylpentane	1,2-Ethanediamine
Cyclopentane	<i>n</i> -Methylethyleneimine
Methylcyclopentane	Pyridine
1,1-Dimethylcyclopentane	Piperidine
1- <i>cis</i> -2-Dimethylcyclopentane	Ethyl nitrate
1- <i>trans</i> -2-Dimethylcyclopentane	Trimethylene sulfide
1-(<i>cis-trans</i>)-3-Dimethylcyclopentane	
Methylcyclohexane	
1- <i>cis</i> -2-Dimethylcyclohexane	
Ethylene	
Propene	
1-Butene	

TABLE I
Results of Initial Experiments

Polymer	Tank gases filtered	Working temp., °C	Air (C), nuclei/cm ³	E/C	
				Ar	Ar-CO
None	no	22	100	110	27
None	yes	22	100	75	22
Polystyrene	no	125	2500	18	5
Polystyrene	yes	125	2700	21	7

TABLE II
Details of Sample Preparation

Polymer	Gas	Temp., °C	Nuclei count,	
			nuclei/cm ³	Collection time
None	FRA ^a	163	100	4 min
	Ar	166	70K	3 min
	Ar-CO	166	30K	5 min
Apiezon C	FRA	160	700K	2½ hr
	Ar	155	5M	2 hr
	Ar-CO	153	500K	2 hr
Polystyrene	FRA	194	200K	1¼ hr
	Ar	188	300K	2 hr
	Ar-CO	189	200K	2 hr

^a FRA = Filtered room air.

A special program was written by Richard K. Sato of the NCAR Computing Facility to normalize the data by removing the instrumental background and the appropriate gas spectrum and adding the gas-instrumental background to each scan. The normalization tended to remove from the compounds found: argon, water, nitrogen, oxygen, ammonia, hydrogen chloride, propadiene, propylene, and hydrogen sulfide, listed in decreasing frequency of removal. On the other hand, methane and hydrogen chloride were occasionally added. Nitrous oxide was both removed and added in various individual runs.

The normalized data were also processed in the CDC 6600 computer program.

RESULTS

While the normalization step tended to simplify the computer output, it did not do so sufficiently to change the conclusions reached.

In every sample, CO was detected, indicating that the reaction of CO with the polymer is not quantitative.

Polystyrene is more reactive than the hydrocarbon oil, judging by the variety and amounts of reaction products found, although it must be pointed out that this is almost certainly the result of the approximately 30°C higher temperature at which the polystyrene was pyrolyzed. At compa-

rable temperatures, polystyrene produces many fewer nuclei than does hydrocarbon and hence, presumably, at least fewer products if not also fewer kinds of products.

Saturated, branched, and/or oxygenated species were found most often in the samples prepared in Ar-CO, least often in Ar. Saturates were about twice as common as unsaturates.

The hydrocarbon oil tended to give more branched and/or oxygenated species and fewer saturates than did polystyrene, with no difference in unsaturates.

Despite these differences, the makeup of the computed reaction products does not vary significantly as polymers or gases are changed. While the results are not sufficiently precise for one to even think about performing mass balance or kinetic yield calculations, the makeup of the products is consistent with those to be expected from free-radical reactions.⁸ Species from methane to C₈ were identified, with saturates covering the entire C₁-C₈ range. Unsaturates were limited to the C₂-C₄ range. Branched structures covered the C₄-C₇ range. Oxygenated species were restricted to the C₁-C₃ range. Benzene was identified from polystyrene, as were cyclic C₅ compounds. Ammonia was frequently listed in the computer printout, and a very few organic nitrogen compounds were also listed. These findings are nearly a list of the computer program library, except for the sulfur and some of the nitrogen compounds. No reactive sulfur was found in the gases nor were sulfur compounds listed among the reaction products.

DISCUSSION

The kinds of low molecular weight reaction products found, coupled with their low concentrations, do not strike one as being what are commonly thought of as condensation nuclei; indeed, there is no *a priori* reason for assuming that these nuclei in any way resemble naturally occurring condensation nuclei. Nothing indicative of any process other than the usual free-radical or autoxidative polymer degradation process⁸ was found. No outstanding amounts of carbonyl compounds were identified. The computer program library contained no acids. Unreacted CO was always present. These facts indicate that the CO is not a primary reactant. Of course, the CO may be acting as a carrier, a sort of catalyst, in forming saturated species, in which case the CO would be found free. Because hydrogen peroxide exists as a liquid and decomposes to water and oxygen when gasified, little can be said about this compound even though it was an expected product. The fact that the oxygen to nitrogen ratio was lower than 1:4 further suggests that the peroxide was not present in sufficient quantities to observe and was therefore not a major product.

The inability of the mass spectrometer to resolve small differences in mass presented a challenge to the interpretation of molecular ions of H₂O and NH₃, CO and N₂, and N₂O and CO₂. Identification of individual members of these pairs was accomplished by the computer regression program

using noninterfering parts of the individual cracking patterns. For example, the OH— water peak at m/e 17 covers up NH_3 present, but the ratio $(m/e\ 17)/(m/e\ 18)$ for water is consistently reproducible and can be used to back out the excess m/e 17 contribution from other sources. The NH_3 cracking pattern with peaks at m/e 17, 16, 15, and 14 can then be used to define ammonia present. In a like fashion, CO and N_2 can be differentiated by the 12 and 14 peaks appearing in CO and N_2 , respectively. The contribution of C_2 compounds may be separated from the foregoing pair by fragments in the 25–27 range. Similar procedures separate CO_2 and N_2O . This type of analysis is bound to involve a certain residual which cannot be identified. In all cases, this residual was less than 40 mole-% of the total sample, with an average residual in the 10–15 mole-% range.

Since the compounds found in the gases and reaction products have also been found in photochemical smogs, where some of them are taken to be the gaseous precursors of the atmospheric aerosols formed in such smogs, it might be argued that the condensation nuclei found here may be the solid precursors of these aerosols. The portion of the gas train between the converter and the nuclei detector is stainless steel, thus ruling out a photochemical reaction mechanism similar to that operating in smog formation. The transit time through this portion of the gas train is approximately 1 sec; smog takes hours to form. Nor can a thermal reaction mechanism be invoked, since kT at the operating temperatures used is less than 1% of $h\nu$ for a 3000-Å photon.

An alternate approach to studying the condensation nuclei may be possible. One could use two Millipore 0.45 μm filters. One would have filtered room air passed into it from a warm but empty converter for 8-hr to give a system blank. The other would have filtered room air passed into it from a warm converter containing polymer for 8 hr. It is hoped the latter will have retained enough nuclei to be differentially detectable from the first filter after the filters are separately dissolved in a suitable solvent system and introduced into the mass spectrometer.

CONCLUSIONS

The present attempt to elucidate the mechanism by which CO depresses the production of condensation nuclei from warm polymers has not been successful. The fault does not appear to lie in the experimental method selected but in the unsuitability of some of the materials. It is altogether probable that scientists better versed in polymer chemistry and in mass spectra interpretation, and using cleaner gases, will be able to elucidate the mechanism successfully.

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