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Variation of the activity of ice nuclei upon exposure to ammonium ion and iodine

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ABSTRACT

Laboratory experiments were performed to determine the extent to which the ice nucleating abilities of several compounds are influenced by the presence of iodine in different forms. Changes were observed in both freezing (liquid phase) and depositional (vapor phase) ice nucleation abilities of a number of lead nucleant-iodine combinations. Iodine vapor increased the number of deposition nuclei per gram of lead oxide by one order of magnitude. Thermodynamic considerations suggest that at least three other lead compounds may respond similarly to iodine vapor. Freezing nuclei active at -1°C were produced from lead oxide particles in the presence of NH_4I; a sensitivity to the temperature prehistory of this system was noted and a qualitative explanation is advanced.

1. Introduction

1.1. Background

Although conditions for homogeneous nucleation may be met in the troposphere, it is generally recognized that nucleation of ice particles is most likely to occur by a process of heterogeneous nucleation. For this reason, the properties of aerosols and their modes of interaction with water become important to the understanding of natural ice forming processes in the atmosphere. At present at least four ways by which particulates can initiate ice are generally recognized (Vali, 1985), yet the relative importance of these mechanisms to ice formation under differing atmospheric conditions is poorly understood and it is only recently that attempts have been made to differentiate the conditions under which their contributions to ice formation are applicable (Plooster and Fukuta, 1975: Pruppacher and Klett, 1980; Manton, 1983).

The ability of insoluble particulates to act as ice nuclei has been widely studied. The role of soluble particles in affecting immersion nucleation has been less thoroughly investigated. Reischel (1973), Reischel and Vali (1975), and Reischel (1984) have reviewed and investigated the case in which a soluble component is present in a droplet frozen by an insoluble immersion nucleus. These studies showed that changes of up to 4°C in supercooling requirement of the nuclei can be expected for conditions found in the atmosphere.

1.2. Lead and iodine as ice nuclei

Iodine particulates may act as ice nuclei at temperatures between -10 and -20°C (Bryant et al., 1959; Ueno, 1984). Rosinski and Parungo (1966) found that various terpenes (and other tree oils) from forested areas react with iodine to form very active ice nuclei. Lead iodide has been shown to be an active deposition nucleus and to act efficiently in both a diffusion and mixing cloud chamber (Mason, 1971; Ueno, 1984). Schaefer (1966) proposed that urban areas could serve as sources of ice nuclei if sufficient iodine were present to combine with lead particulates from automobile exhaust and produce lead iodide. Schaefer (1966, 1968a) suggested sources of iodine and that the active particles are deposition rather than immersion nuclei (1968b). Morgan (1967), Morgan and Allee (1968), and Parungo and Rhea (1970) found that iodine added to a

combustion aerosol (from leaded gasoline) produced active ice nuclei.

Langer (1970) observed condensation-freezing nuclei at the top of the Denver haze layer and proposed that lead bromide compounds (decomposed to lead oxide due to nitrogen oxides and ultra-violet light) acted as the ice nucleant. Moyers et al. (1971) found polluted urban air to contain enough iodine to convert all of the lead found to lead iodide. O'Reagan et al. (1982) suggest that not all the lead particles will be in a reactive form so that conversion to lead iodide may be more important as a downwind effect than as an urban effect. Borys and Duce (1979) found a slight positive correlation between ice nuclei and lead at Providence, Rhode Island.

Grant and Corrin (1973) showed that conversion of lead chlorobromide to lead iodide is thermodynamically unfavorable and found that the ice nuclei observed when auto exhaust is exposed to iodine were not due to this reaction but the product of iodine with an unidentified constituent.

The production of ice nuclei in the atmosphere from iodine and certain lead containing aerosols could proceed by the interaction of iodine vapor with the aerosol particles. The possibility also exists for interaction to occur after the lead aerosol and the iodine have become incorporated into liquid water, specific examples are demonstrated below.

2. Experimental

2.1. Materials and preparations

Nucleants, iodine and soluble salts used in these tests were all of analytic reagent grade; salt concentrations reported are molal, m = g salt per Kg H_2O. A number of the nucleants were similar in composition to those reported to be present in automobile exhaust (TerHaar and Bayard, 1971; O'Reagan, 1982). Immersion nucleants were prepared as hydrosols by adding the dry powder to the solutions at a concentration of 10^{-3} g nucleant per g H_2O just prior to use. Solutions were prepared with distilled, deionized water which had a minimum resistivity of 10 megohm. The water and solutions were filtered through 0.025 μm filters before use and exhibited nucleation temperatures that were lower than those of the hydrosols made with distilled water only. Deviations from these procedures are described with the specific test.

For deposition nucleus tests, the nuclei were collected on the surface of membrane filters by passing known volumes of hydrosols through filters of 0.45 μm pore size with subsequent drying in a laboratory desiccator. Background tests (to determine contributions by distilled water and the filter surface) were conducted with each test; these counts were subtracted from the total nucleus count.

2.2. Measurements

The method of determining the immersion nucleation temperatures has been described previously (Vali, 1971; Reischel, 1978). It consists of placing a matrix of drops (typically, 100 hydrosol and 10 distilled water control drops) on a silicone resin coated cold stage (cooled at a constant rate of 2.5°C/min) and determining the freezing temperatures of the drops. T_{10} and T_{90} correspond to supercoolings (°C) at which 10% and 90%, respectively, of the drops froze. When corrected for equilibrium melting point depressions, these are termed true supercoolings (TS_{10} and TS_{90}). A minimum of two tests was made for each temperature reported; results typically agreed to within 1°C. Reliability of the drop freezing method has been discussed previously (Reischel, 1984). It should be noted that ice nucleation rates were not addressed in this study. These freezing rates were assumed to be much less than those induced by the relatively rapid cooling rate used.

Depositional ice nucleation activity was determined using the method of Huffman (1973). Filters containing the nucleant particles are placed on a layer of heavy oil (contained in a depression) at the surface of the lower plate of a static thermal diffusion chamber. The sample tray, at room temperature, is inserted into the chamber and allowed to cool to the upper plate temperature. A temperature difference (ΔT) is then applied to achieve the desired water vapor pressure at the lower plate. A period of 45 minutes was required to grow the crystals to an observable size for counting. The saturation ratio with respect to water (S_w) at the filter surface is given by:

$$S_w = \frac{e_i}{e_w}, \qquad (2.1)$$

where e_i is the vapor pressure of ice at temperature $T + \Delta T$, and e_w is the vapor pressure of water at temperature T. $S_w = 1.0$ was used for all tests and was determined from T, ΔT, and standard tables of saturation vapor pressure over water and ice. The upper and lower plate surface temperatures were regulated to ± 0.01 °C and chamber humidity could be controlled to about 1% (Huffman, 1973). The number of active nuclei per gram of nucleant, N, was determined by counting the number of ice crystals formed, subtracting the background count, and dividing by the known mass (M_n) of the nucleant:

$$N = \frac{N_s - N_b}{M_n}, \tag{2.2}$$

where subscripts s and b represent sample and background, respectively at a given temperature (T) and S_w.

3. Results

3.1. *Immersion nucleation tests*

3.1.1. Insoluble lead compounds. To test PbO particles as immersion ice nuclei in the presence of iodine vapor two techniques were used: (1) dry method, PbO (y) powder was placed in a sealed glass container for 48 h in contact with vapor (at 25 °C) from iodine crystals, the powder was then tested in distilled water; (2) wet method, PbO (y) powder was added directly to iodine saturated distilled water and tested immediately. Saturation was achieved by placing iodine crystals in the water (at 25 °C) several days prior to the tests. The results of the immersion freezing tests are shown in Fig. 1. The iodine treatments altered the activity of the particles by at most a factor of 2; more immersion nuclei were produced by the dry method, while the wet method deactivated the PbO slightly.

To test the effect of iodide ion rather than dissolved iodine on the immersion nucleation activity of lead compounds, tests were performed using 10^{-3} and 10^{-1} m salt concentrations as shown in Table 1. In contrast to the results with NH_4I solutions (Reischel, 1975), KI solutions failed to enhance the activity of PbO (y) or PbO (r); the effects of 0.01 m KI on $PbSO_4$ and PbS were smaller than those of 0.01 m NH_4I. Also shown in Table 1 are the results of tests with PbI_2

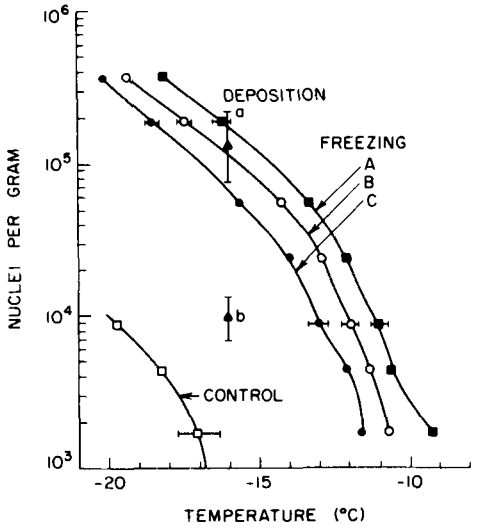

Fig. 1. Immersion (freezing) and deposition ice nucleating activity of PbO. Immersion activity of iodine treated PbO: (A) dry method (solid squares); (C) wet method (solid circles). Immersion activity of PbO in distilled water is shown at (B) (open circles); distilled water saturated with iodine (control) is shown with open squares. Mean deposition activity (solid triangles) of PbO treated with iodine (a) and untreated (b). Bars on data points represent ranges of observations.

(10^{-4} g/g solution) in 0.1 m NaI, NH_4I, $(NH_4)_2SO_4$ and distilled water. These results suggest that the iodide or ammonion ion alone

Table 1. *Supercooling† of lead compounds in iodide and ammonium salts of differing concentrations*

		Concentration (m)			
Nucleant	DW‡	Salt	10^{-3}	10^{-2}	10^{-1}
PbO(y)*	22.0	KI	21.7	21.4	23.0
		NH_4I	21.9	21.0	0.8
PbO(r)*	17.4	KI	–	–	18.6
		NH_4I	19.8	13.4	1.0
		NH_4NO_3	–	–	24.4
$PbSO_4$	24.7	KI	23.6	8.4	–
		NH_4I	24.3	2.6	1.9
PbS	23.6	KI	18.0	17.9	–
		NH_4I	19.2	13.6	3.0
		NaI	–	–	13.4
PbI_2	22.6	NH_4I	–	–	1.8
		$(NH_4)SO_4$	–	–	23.0

† T_{90} in °C.
‡ DW = distilled water.
* PbO from two different sources: y = yellow, r = red.

cannot be responsible for the activation of lead compounds in NH_4I solutions; rather, a requirement of the presence of both these ions is suggested.

In 0.1 m NH_4I, lead zirconate ($PbZrO_3$) exhibited a change in T_{90} from 23.1°C in distilled water to 1.1°C; for lead titanate ($PbTiO_3$) the corresponding T_{90}'s were 21.4°C and 5.5°C. Both of these lead compounds are extremely insoluble in water.

Further testing revealed an interesting property of the PbO-NH_4I system; it is sensitive to the temperature pre-history of the system. A set of drops containing PbO(y) in 0.1 m NH_4I was placed on the cold stage (initially at +15°C) and T_{90} determined. After all the drops had frozen the stage was warmed to +0.5°C for 5 minutes to melt the drops. Upon subsequent cooling, the drops froze at temperatures slightly warmer than initially. On each of 13 successive refreezings the melting temperature was raised by 0.5°C. During this procedure, T_{90} fell to about 4.9°C in a fairly uniform manner and remained fairly constant. The melting temperature after the 14th freezing was +0.5°C; for 5 more refreezings the melting temperature was varied, as shown in Fig. 2. When the drops were heated and melted above about +1°C very active nuclei did not occur. This activation appears similar to that due to the formation of ice in capillaries (Edwards et al., 1970); however, it is not a likely explanation of the high initial activity. The T_{90} exhibited after melting at temperatures > +3°C, is similar to that observed for PbI_2 (Reischel, 1975).

A similar test sequence was also made using this nucleant-salt combination; but the hydrosol was first filtered through a 5.0 μm pore filter and the melting temperature was +0.6°C between freezings. T_{90} for the first freezing was 16.0°C; those for the second through sixth were, respectively, 5.7, 7.1, 6.9, 6.7 and 6.3°C. After the sixth freezing, melting at +16.1°C gave a subsequent T_{90} of 10.4°C. The very active nuclei found previously did not occur, suggesting that large PbO particles are required to form the most active immersion nuclei. Analysis of the PbO(y) sample using an automatic hydrosol particle size analyzer (Behringer, 1975) showed that the sample had a mean diameter of 5.6 μm and a median diameter of 6.8 μm.

PbI_2 was also tested in water of pH = 2(HNO_3),

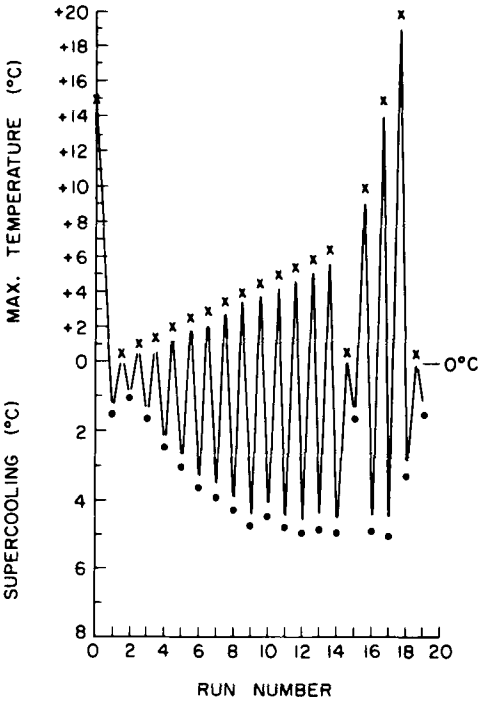

Fig. 2. Supercooling (T_{90} in °C, solid circles) as a function of maximum melting temperature (x) for repeated freezing of PbO in 0.1 m aqueous NH_4I.

and pH = 11 (KOH). The respective T_{10}/T_{90} values obtained were 5.1/7.1 and 14.8/17.4°C. A high hydroxyl ion concentration apparently impairs the immersion nucleation activity of PbI_2; and may relate to the formation of $Pb(OH)_2$ at the nucleant surface.

The above results suggest that the most active nuclei were not simple PbI_2. In fact, it was found that at least two different compounds can be obtained from systems containing PbO and NH_4I (see below).

3.1.2. Soluble compounds. To test the effect of the Pb^{2+} ion on immersion nucleation, lead nitrate was used as a representative lead (II) salt at concentrations ranging from 10^{-8} m to 10^{-2} m in combination with three naturally occurring nucleants kaolin (KLN), mica (MCA) and one (LDN) derived from decayed deciduous leaf matter (Schnell and Vali, 1972). The T_{10} and T_{90}'s are shown in Table 2; no large changes in supercooling were observed.

Solutions of NH_4I and KI (at 0.1 m) were

Table 2. *Supercoolings of hydrosols containing Pb^{2+} (as lead nitrate): for each nucleant, the upper line is T_{10}; lower line is T_{90} (in °C)*

	Concentration of $PbNO_3$(m)								
Nucleant	DW*	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}
DW*	**	22.3	22.6	21.5	20.6	20.5	21.1	18.9	22.8
		26.9	27.5	25.8	26.8	26.3	26.1	26.5	27.7
KLN	16.0	15.5	15.4	15.0	14.3	14.4	16.6	16.5	–
	21.0	21.0	20.7	20.6	20.8	21.1	21.1	20.7	–
MCA	10.7	–	–	–	12.0	12.0	13.6	16.1	–
	17.7	–	–	–	20.3	21.2	21.8	20.0	–
LDN	6.3	5.7	6.3	6.5	6.6	6.7	6.7	7.0	–
	9.0	8.9	8.8	8.8	9.1	9.3	9.5	9.6	–

* DW = distilled water.
** No nucleant intentionally added.

Table 3a. *Supercoolings of mixtures of 0.1 m iodides with $Pb(NO_3)$: for each nucleant the upper line is T_{10}; lower line is T_{90} (°C)*

	Concentration of $PbNO_3$(m)			
Salt	10^{-6}	10^{-5}	10^{-4}	10^{-3}
DW	21.5	20.6	20.5	21.1
	25.8	26.8	26.3	26.1
NH_4I	15.9	14.5	1.5	6.5
	20.0	16.4	2.5	11.0
KI	20.9	18.0	6.4	12.7
	24.8	23.6	9.9	16.6

Table 3b. *Supercoolings of PbI_2 and $PbBr_2$ in distilled water: for each nucleant the upper line is T_{10}; lower line is T_{90} (°C)*

	PbX_2(g/gH_2O)			
X	5×10^{-3}	1×10^{-3}	5×10^{-4}	1×10^{-4}
I	5.5	4.5	6.6	15.5
	7.1	5.6	8.0	22.6
Br	12.2	–	–	9.4*
	15.3	–	–	10.2*

* 1.8×10^{-4} m = concentration $PbBr_2$.

tested after mixing with solutions of varying concentrations of $PbNO_3$. For the same concentration of iodide ion, nuclei produced using NH_4I were more active (Table 3a). In an excess of iodide ion, the lowest T_{90} was found at a concentration of Pb^{2+} that is considerably below that expected from the solubility of PbI_2 in water (1.6×10^{-3} m; Linke, 1965) and yet well above that reported for the solubility of PbI_2 in 0.1 m KI (4.2×10^{-5} m; Linke, 1965). Values for the solubility of PbI_2 in 0.1 m NH_4I are not available, but at 0.2 m NH_4I the solubility is 6.4×10^{-4} m (Linke, 1965). The solubility data for KI show (and those for NH_4I suggest) that the solubility of PbI_2 passes through a minimum at an iodide concentration of 0.1 m.

Both PbI_2 and $PbBr_2$ are slightly soluble in water; 4.4×10^{-4} g/gH_2O and 4.6×10^{-3} g/gH_2O at 0°C, respectively (Linke, 1965), and were tested in distilled water to observe the effects of solubility on their immersion nucleation activity. The results show (see Table 3b) that PbI_2 exhibits a higher activity (smaller T_{90}) at a concentration above its solubility limit; as expected the activity drops off at a concentration below its solubility limit.

TiO_2 and titanates of various types occur as fairly widespread minor mineral constituents of the earth's crust (Clark, 1973). Tests conducted with titanium dioxide (TiO_2) and barium titanate ($BaTiO_3$) are reported here and include a number of nitrates as the soluble component since NO_x is commonly associated with polluted atmospheres

Table 4. *Supercoolings of TiO_2 and $BaTiO_3$ in different soluble salts: for each nucleant the upper line is T_{10}; lower line is T_{90} (in °C)*

Nucleant	Concentration (m) DW	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}
				LiI			
TiO_2	11.1	10.3	10.2	10.3	10.1	9.8	7.3
	13.7	13.0	12.9	13.2	12.7	13.4	13.4
				$Ba(NO_3)_2$			
TiO_2		10.7	11.0	10.7	10.5	10.6	11.0
		13.7	13.8	13.9	13.8	13.8	14.2
$BaTiO_3$	16.0	18.5	16.7	15.1	17.3	18.1	17.6
	22.6	22.6	22.5	21.9	22.6	22.6	23.6
				$Zn(NO_3)_2$			
TiO_2		10.4	–	10.5	–	–	11.5
		13.7	–	13.6	–	–	15.4
$BaTiO_3$		17.9	16.0	16.3	16.2	14.8	15.5
		22.7	22.2	21.8	22.0	20.8	21.7
				$Fe(NO_3)_3$			
TiO_2		–	–	–	–	–	12.4
		–	–	–	–	–	15.4
$BaTiO_3$		17.8	15.7	20.6	21.2	22.6	23.5
		22.5	22.3	23.7	25.0	25.5	26.2

Table 5. *True supercoolings* of TiO_2 and $BaTiO_3$ in 0.1 m nitrates: for each cation, TS_{10} is numerator; TS_{90} is denominator (in °C)*

Nitrate	TiO_2	$BaTiO_3$
DW	11.1/13.7	16.0/22.6
Fe^{3+}	12.2/15.2	23.3/26.0
Cr^{3+}	11.3/14.2	20.6/24.5
Mg^{2+}	10.9/14.1	–
Ni^{2+}	11.5/14.7	17.6/23.1
Cu^{2+}	11.3/14.5	18.0/23.5
Zn^{2+}	11.3/15.2	26.4/23.4
Co^{2+}	11.3/14.6	20.2/23.4
Li^+	7.1/13.2	–
Ba^{2+}	10.8/14.0	17.4/23.4
K^+	10.8/14.2	20.1/23.3
NH_4^+	10.8/13.9	17.6/22.6

* Supercoolings corrected for melting point depression (see text).

and is produced by lightning discharges. TiO_2 is little affected by the soluble nitrate nor is $BaTiO_3$ (see Tables 4 and 5).

3.1.3. Characterization of active lead immersion nuclei. The PbO-NH_4I system described above produced some of the most active immersion nuclei observed during the course of these studies and exhibited evidence that changes in the nucleant were occurring. Two separate approaches were taken to characterize the physical and chemical nature of the changes observed; electron microscope studies and chemical analysis of the products of mixtures of NH_4I and PbO.

Viewing of the hydrosol particles under a transmission electron microscope was pursued to detect differences in particle morphology. To obtain particles representative of those which acted as immersion nuclei, the hydrosols were cooled to 0°C and centrifuged for ten minutes. Water exposed particles are shown in Fig. 3a; those prepared in 0.1 m NH_4I are shown in Fig. 3b. Particles exposed only to water appeared to be hexagonal plates or pyramids and exhibited a definite ring (or density gradient) about their perimeter. The NH_4I exposed particles were fewer in number, showed skeletal outlines about the particles, and often had numerous satellite particles. These results suggest that the PbO in water precipitated a light ring of material about the original particles upon cooling to 0°C, while those placed in 0.1 NH_4I dissolved in the solution. Fig. 3c and 3d show the results of similar treatments given to $PbCO_3 \cdot Pb(OH)_2$ particles; these particles exhibited needles in addition to satellite particles. The presence of simple hexagonal PbI_2 is not suggested by these tests.

During immersion freezing tests lead nucleants in 0.1 m NH_4I underwent a series of color changes; turning first pale yellow, then bright yellow and finally a pale yellow as the temperature was lowered. By dissolving PbO in ammonium iodide solution differently colored materials were obtained and characterized using standard wet chemical analysis procedures; the isolated compounds were then tested for immersion nucleation activity. Two different methods were used to dissolve PbO in ammonium iodide solutions: evaporation and heating.

The first method consisted of placing 0.1 m NH_4I solution over a large amount of PbO (*y*) and evaporating the liquid at room temperature (~25°C). A few hours after initial mixing, the PbO turned white on the surface with small patches of yellow appearing as evaporation pro-

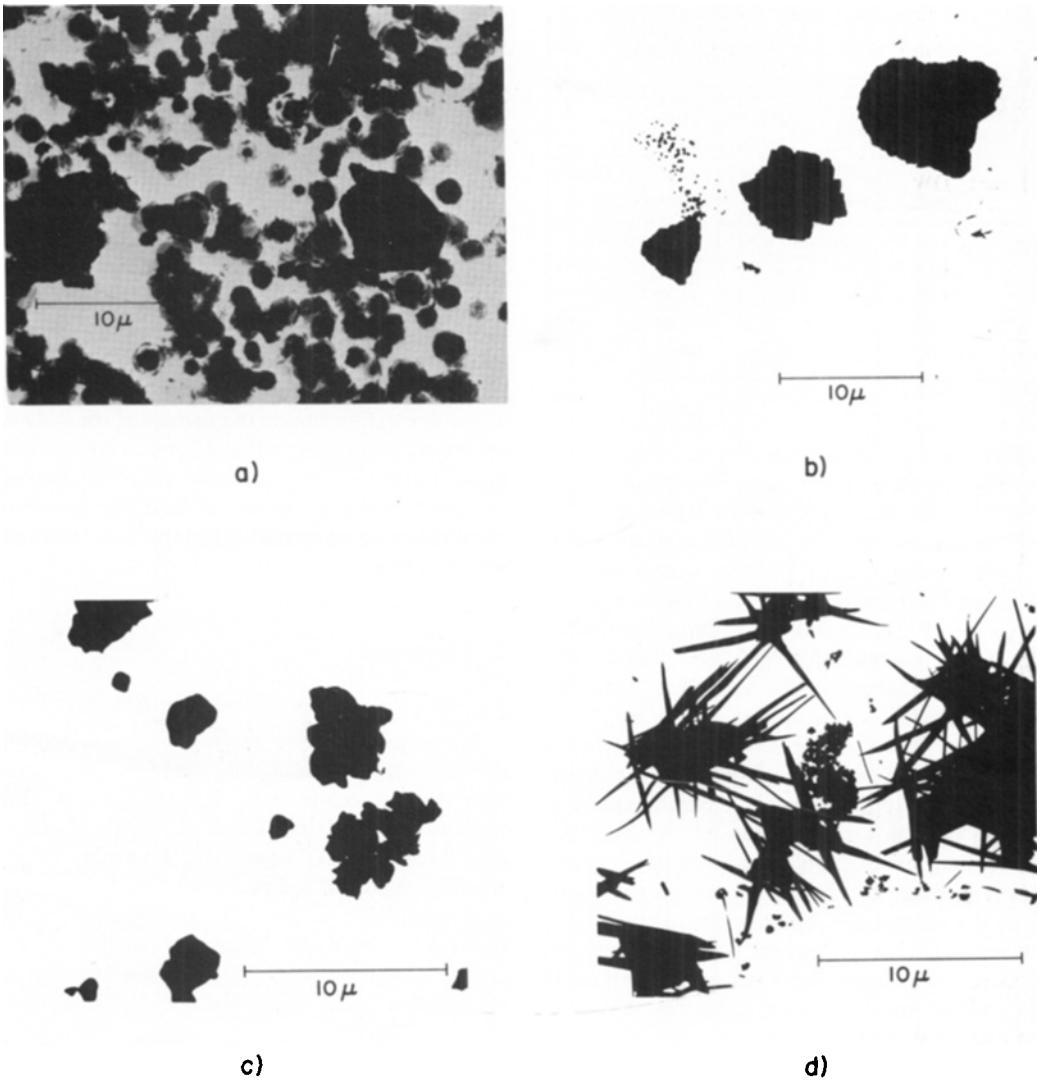

Fig. 3. Transmission electron microscope photographs of lead particles: (a) PbO water exposed; (b) PbO exposed to 0.1 m NH_4I; (c) $PbCO_3 \cdot Pb(OH)_2$ water exposed; (d) $PbCO_3 \cdot Pb(OH)_2$ exposed to 0.1 m NH_4I.

gressed. In less than 24 hours clusters of fine yellow needles appeared; less than 1% of the PbO remained. On heating, the PbO dissolved completely and upon cooling yellow needle crystals appeared. When the needle crystals were placed into distilled water they decomposed giving a bright yellow precipitate which had an immersion nucleation activity similar to that of PbI_2 ($T_{10}/T_{90} = 4.8/6.5$°C) but considerably less than that of PbO in 0.1 m NH_4I. A similar mixture of PbO in 0.1 m KI did not change on evaporation; no nucleation tests were conducted.

A large quantity of the needle crystals was prepared and analyzed for Pb^{2+}, NH_4^+, I^- and water. The results, (see Table 6) correspond to an empirical formula of NH_4PbI_3 with some water of hydration. A formula of $NH_4PbI_3 \cdot H_2O$ seems reasonable to describe this compound.

Demassieux (1923) reports the existence of a "double-salt" of $PbI_2 \cdot NH_4I \cdot 2H_2O$. Iiyasov et al.

Table 6. *Theoretical and experimental NH_4^+, I^-, Pb^{2+}, H_2O contents (in %) for NH_4PbI_3 and $NH_4PbI_3 \cdot \times H_2O$*

	NH_4PbI_3		$NH_4PbI_3 \cdot H_2O$		
	Theory	Found	Theory ($\times = 1$)	Found	Theory ($\times = 2$)
NH_4^+	2.97	3.70	2.89	3.54	2.81
I^-	62.87	64.53	61.02	61.76	59.31
Pb^{2+}	34.16	31.47	33.20	30.12	32.27
H_2O	-	-	2.24	4.24	5.61
Total	100.00	99.70	100.00	99.66	100.00

(1969) lists powder pattern *d*-values (unindexed) for several other lead halide complexes. Abel (1973) reports that a pale yellow $KPbI_3 \cdot 2H_2O$ is well known and that an anhydrous white $KPbI_3$ (which decomposes to PbI_2 in water) may be obtained from the hydrate. The Powder Diffraction File (1975) lists powder patterns for $CsPbI_3$ and $KPbI_3$ but none for NH_4PbI_3. The *d*-value obtained for the needles described here are reported in the powder diffraction file, set 30.

Single crystal X-ray data was obtained but the largest needles were quite small; the patterns were weak. From the rotation photograph a c-spacing of 0.46 nm was deduced. A zero level Weisenberg photograph (22 h) was taken and a repeat distance of about 1.13 nm was deduced from the central line on this photograph. By a process of trial and error, the powder pattern has been tentatively indexed with an orthorhombic unit cell of dimensions $a = 1.486$ nm, $b = 1.115$ nm and $c = 0.465$ nm.

A white precipitate was obtained when 2.511 g of PbO were added to 250 ml of 0.1 m NH_4I and stirred at 80°C for 3 h. This precipitate was separated and dried; the powder pattern was rich in lines and indexing was not attempted. This material does not decompose in water and its nucleating ability is considerably poorer than that of PbI_2; $T_{10}/T_{90} = 9.2/13.0$°C.

3.2. *Deposition nucleation tests*

Two sets of twelve filters were prepared (with PbO (*y*) nucleant). One set (b) was tested after drying in room air for one hour, the other set (a) was exposed for one hour to iodine vapor at its equilibrium vapor pressure (at ~25°C) in a sealed glass container before testing. Deposition nucleation tests were conducted separately for each set at −16°C. Exposure to iodine vapor increased the number of nuclei per gram of PbO by about one order of magnitude (see Fig. 1).

Iodine absorption on particulate materials is a complex process and for many materials is at least partially reversible (Clough et al., 1965). Additional tests showed that the length of exposure to room air after iodine treatment correlated with a drop in the number of deposition nuclei obtained. Whether this drop was due to exposure to the room air or the iodine was physisorbed rather than chemisorbed (Adamson, 1967) at the active nucleation site on the surface of the PbO is uncertain. However, when iodine crystals were placed directly into the test chamber during processing results similar to those for (a) were obtained, suggesting that the activation observed was complete.

4. Discussion

4.1. *Reactions of lead and iodine compounds*

While the primary composition of lead aerosol particles from automobile exhaust are lead chlorobromo compounds, lead oxide has also been observed (Hirschler et al., 1957; Terhaar and Bayard, 1971; Boyer and Laitinen, 1975). The first report of iodine-auto exhaust ice nuclei suggested lead oxide as the parent solid (Schaefer, 1966) and laboratory studies of ice crystals suggested that lead oxide was involved in the production of active ice nuclei (Cheng and Hogan, 1970).

A thermodynamic analysis similar to that of Grant and Corrin (1973) was made for a number of lead compounds and iodine. The free energy for the reactions were calculated from the standard free energies of formation (Keller, 1967; Weast, 1967) at 25°C. The equilibrium constant for the reaction is:

$$K = \exp(-\Delta G^\circ / RT), \tag{4.1}$$

so that if $K > 1$, the reaction is possible. Of the lead compounds considered, only PbO (yellow), PbO (red), PbSe, and PbS have thermodynamically favorable free energies for reaction with iodine (see Table 7). The respective equilibrium constants for these reactions are 6.5, 4.7,

Table 7. *Free energy (ΔG kJ/mole) for the lead compounds considered in this study*

Compound	Free energy
PbS	−100.51
PbSe	−91.51
PbO(y)	−4.65
PbO(r)	−3.81
PbO_2	25.87
$PbBr_2$	74.72
$PbCl_2$	120.89
$Pb(OH)_2$	227.89
Pb_3O_4	424.63
PbF_2	426.12
$PbCO_3$	433.42
$PbSO_4$	618.40
$PbCO_3PbO$	625.56
$PbCO_32PbO$	819.79
$PbSiO_3$	981.07
Pb_2SiO_4	1176.56
$Pb_3(PO_4)_2$	2207.03

1.1×10^{16}, and 4.0×10^{17}, suggesting that PbS is considerably more reactive with iodine and a better candidate for transformation to PbI_2 than is PbO.

$PbBr_2$, ($K < 1$) has been reported to form free lead at its surface upon exposure to daylight and UV radiation when in contact with HBr (Nilsson and Haight, 1966). Free lead at the surface of $PbBr_2$ particles would render them candidates for the formation of PbI_2 in the presence of iodine vapor.

O'Reagan et al. (1982) have suggested that since urban atmospheres contain higher concentrations of sulphate than any iodine species the formation of PbI_2 by precipitation in cloud droplets is only a remote possibility. Winchester and Duce (1966) suggest that oxidation of SO_2 to sulfate by iodine produces iodide ions which remain with the ammonium sulfate. Other species can be oxidized in aqueous solution by dissolved iodine (e.g., $2Fe^{2+} + I_2 \rightarrow 2Fe^{3+} + 2I^-$); these may also contribute to the formation of iodide ion in aqueous solution droplets. Reischel (1975) has shown that a number of lead compounds (including $PbSO_4$, this study) become very active immersion nuclei in ammonium iodide solutions; the mechanism for this synergistic effect is discussed below.

4.2. Summary

The above tests have shown that the presence of iodine vapor can increase the number of deposition nuclei per gram of lead oxide at −16°C and 100% RH by one order of magnitude. The results presented here also suggest that, for PbO at least, the activation decreases upon removal of the iodine source. Thermodynamic considerations show that PbO, PbSe, and PbS have favorable free energies for conversion to PbI_2 in the presence of iodine vapor.

Immersion nuclei active at temperatures as warm as −1°C were produced in hydrosols of lead compounds in ammonium iodide solutions. The co-presence of both the ammonium and the iodide ion in solution was shown to be required to produce these very active nuclei from lead compounds. The results suggest that a surface reaction or compound formation occurs in these hydrosols to produce very active immersion nuclei. Study of compounds obtained from lead oxide hydrosols suggest that a complex salt hydrate may be responsible for the improved immersion nucleation activity of lead (II) compounds in 0.1 m NH_4I. At least one complex salt of AgI and NH_4I has been shown to have a crystal structure very close to that of ice and also exhibit excellent ice nucleating properties (Davis et al., 1975). It is possible that patches of the complex salt hydrate (described above) form on the surface of PbO (and other lead (II) compounds) in 0.1 m NH_4I and improve the ice nucleating ability of the hydrosol.

The PbO-NH_4I system exhibits a dependence on the prehistory of the nucleating system. Dependence of nucleation temperature on prehistory has been observed by Wada and Matsuo (1984) for sodium acetate trihydrate, a material which exhibits large supercoolings. To explain their results, they have used the crystalline absorption model proposed by Richards (1932). In this model, the heat of absorption and melting temperature of a crystalline absorbate is higher than that of the pure liquid absorbate. Once formed, the crystalline absorbate may be deactivated by heating above its melting temperature. Here, PbO offers the absorbent for which the heat of absorption of a crystalline absorbate (perhaps $NH_4PbI_3 \cdot 2H_2O$) may be higher than that of the liquid absorbate (water). The crystalline absorbate does not fuse at the ordinary melting point

of ice but preserves its crystallinity above 0°C. The crystalline absorption model offers a satisfactory qualitative explanation of the reactivation and deactivation of the nucleating abilities of the PbO-NH_4I system with temperature. It remains for future experiments to give a quantitative explanation of these phenomenon and to explore the possible existence of other such systems of relevance to ice formation in the atmosphere.

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6. Appendix. List of symbols

S_w = saturation ratio with respect to water
e_i = saturation vapor pressure over ice
e_w = saturation vapor pressure over water
T = temperature
ΔT = temperature difference
N = number of active nuclei per gram of nucleant
N_s = number of nuclei found for a given test
N_b = number of nuclei found due to filter background
K = equilibrium constant
ΔG° = standard free energy of formation from element
R = ideal gas constant

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