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To: All Members of the LIA Health and Safety Committee

Re: Additional information on leaded gasoline and production of condensation nuclei in the atmosphere

Attached for your information is a copy of an article from the current issue of Science which is the latest report in the continuing investigations by the Atmospheric Sciences Research Center, State University of New York. You will remember last year's article by Professor Schaefer of this university in which he claimed to have measured condensation nuclei in the upper atmosphere resulting from the interaction of lead from gasoline with i Jine vapor. (*)

I would be most interested in your comments on this work and whether or not you have any suggestions which might lead to action on our part. At the present time we are merely following with interest these developments.

Very truly yours,

Don C. Fowler

DCF:sw
attachment

(*) "Ice Nuclei from Automobile Exhaust and Iodine Vapor", Vincent J. Schaefer, Science, vol. 154, 23 December 1966, pp. 1555-1557.

Lead Ahead with Lead

Ice Nuclei from Direct Reaction of Iodine Vapor with Vapors from Leaded Gasoline

Abstract. *Large numbers of ice nuclei, active at −15°C or colder, can be generated by mixing vapors from leaded gasoline with iodine vapor. This reaction will produce 10^6 Aitken nuclei per cubic centimeter in a closed system with a volume of 2 liters. When unleaded gasoline is substituted, no nuclei of either type are detectable.*

Schaefer (*1*) has shown that ice nuclei can be generated by exposing products of automobile exhausts to iodine vapor. My experiments show that ice nuclei, active at −15°C or colder, can also be generated by direct reaction of iodine vapor with vapors resulting from the evaporation of leaded gasoline. Whereas gaseous reactions forming condensation nuclei are quite well known, this is the first case in which the mixing of two gases has been shown to generate freezing nuclei.

Vapors from leaded gasoline, introduced to the cold chamber of an Int AR Bailey (*2*) ice-nucleus counter, after passing over the surface of a solution (1.5 g per liter) of iodine in mineral oil at room temperature, produce a large number of ice crystals in about 90 seconds. Activity is substantial at −15°C and rises sharply at −19° to −20°C. It was not possible to evaluate activity at temperatures warmer than −15°C with the equipment available at the field laboratory.

A significant background of iodine-activated nuclei, even in the rural environment of our field laboratory, necessitated the use of a filtered input to demonstrate that the increased number of ice crystals detected was due to the addition of gasoline vapors. Admission of 1 liter of a mixture of air and leaded gasoline vapor with iodine vapor produced about 10^6 ice crystals at −20°C over a 15-minute period. Repetitions of this experiment with "clean" unleaded gasoline did not produce ice crystals at a temperature of −20°C.

A smaller, but still significant, number of ice crystals can be generated by placing a container of leaded gasoline near the entrance to the filter when iodine vapor is present in the system. The ability of these vapors to penetrate a filter and still form ice nuclei requires a thorough investigation to determine what methods can be used to eliminate the influence of these vapor-induced nuclei from future experiments with a cloud chamber.

Substitution of an Aitken nucleus counter for the ice-nucleus counter yields an impressive result, as more than 10^6 nuclei per cubic centimeter, active at 1.2 expansions, can be detected in the reaction bottle. A bottle with a capacity of at least 2 liters must be used because a short residence time is required for the reaction to take place and for the particles to grow to a size sufficiently large to be detected by the Aitken counter. When unleaded gasoline is substituted for leaded gasoline, no particles can be detected.

These experiments provide additional evidence that not only products from automobile exhausts, but also those from evaporation of leaded gasoline, are effective ice nuclei in the presence of iodine vapor. Because evaporative losses from the carburetor and gas tank can amount to as much as 8 percent of total automotive emission, this can be a significant source of atmospheric lead and freezing nuclei.

AUSTIN W. HOGAN
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1. V. Schaefer, *Science* 133, 1395 (1961).
2. G. Langer, J. Rosinski, C. F. Edwards, *J. Atmos. Sci.* 8, 116 (1963).
3. Supported by

Polymerization of Hemoglobin of Mouse and Man: Structural Basis

Abstract. *Human hemoglobin Porto Alegre and mouse hemoglobin (BALB/cJ) polymerize by forming intermolecular disulfide bridges. Both hemoglobins have externally oriented reactive cysteinyl residues in the β-chains of the beta chains. Hemoglobin Porto Alegre can be designated as $\alpha_2\beta_2^{6\,Val}$. The cysteinyl residue of the mouse hemoglobin is in position 13 in the beta chains.*

Hemoglobin that polymerizes occurs frequently in amphibians and reptiles (*1*), they also occur in certain mice (*2*) the macaque (*3*), and in one Caucasian family (hemoglobin Porto Alegre) (*4*). Polymerization of amphibian, reptilian, and mouse hemoglobin occurs by formation of intermolecular disulfide bridges, usually after hemolysis (*5*). Measurements of oxygen equilibria in hemoglobin from the bullfrog, snapping turtle, and certain mice indicate that oxygenation is not changed by polymerization (*6*).

We have now determined the position of the cysteinyl residues responsible for the polymerization of both human hemoglobin Porto Alegre and BALB/cJ mouse hemoglobin. Each hemoglobin contains a reactive cysteinyl residue near the NH$_2$-terminus of its β-chain, β-9 in Porto Alegre and β-13 in BALB/cJ. Residues at both positions are at the surface and are oriented outward according to the tentative atomic model of hemoglobin (*7*). Hemoglobin Porto Alegre is one of five known human hemoglobin variants which have amino acid substitutions that do not change the number of ionizable groups. The others are hemoglobins Köln (β 98 Val → Met), (*8*), Genova (β 10 Leu → Pro), Kansas (β-102 Asn → Thr), and Freiburg (β-21 Val → O) (*9*). Each of these was discovered because the change affected its physiological properties, stability, or electrophoretic mobility. All other known variants (about 50) involve substitutions which alter the number of ionizable groups (*10*). We assume that many neutral variants must exist, but appropriate screening techniques for their detection are lacking.

A Porto Alegre hemolysate (*11*), dialyzed against carbon monoxide-saturated 0.2*M* NaCl at 4°C overnight, was applied to a column (2.8 by 70 cm) of Sephadex G-100 (*9*). The polymeric fraction (Fig. 1) had a sedimentation coefficient, $S_{20,w}$, of 9.5. The polypeptide chains were separated in 8*M* urea on carboxymethylcellulose (*12*). Vertical starch gel electrophoresis of the globins at pH 8.9 (*13*) showed that the β-chains were absent from the normal position, while the α-chains appeared unchanged (Fig. 1, inset). Polymerization of BALB/cJ hemoglobin was accelerated by incubation