Apparently these phenomena represent more than just another special subject of physics. There seems to be good reason to suspect that they are manifestations of quantum mechanisms on a macroscopic scale. If this conjecture should prove to be true it would, of course, be a matter of fundamental significance. . . . Here would be a case where quantum mechanisms would directly reach into the macroscopic world.

London would have enormously enjoyed reading about the "Molecule of the Year."

Russell J. Donnelly
Department of Physics, University of Oregon, Eugene, OR 97403–1274, USA

References

1. *Report of an International Conference on Fundamental Particles and Low Temperatures, Vol. II, Low Temperatures* (Physical Society, London, 1947).

■

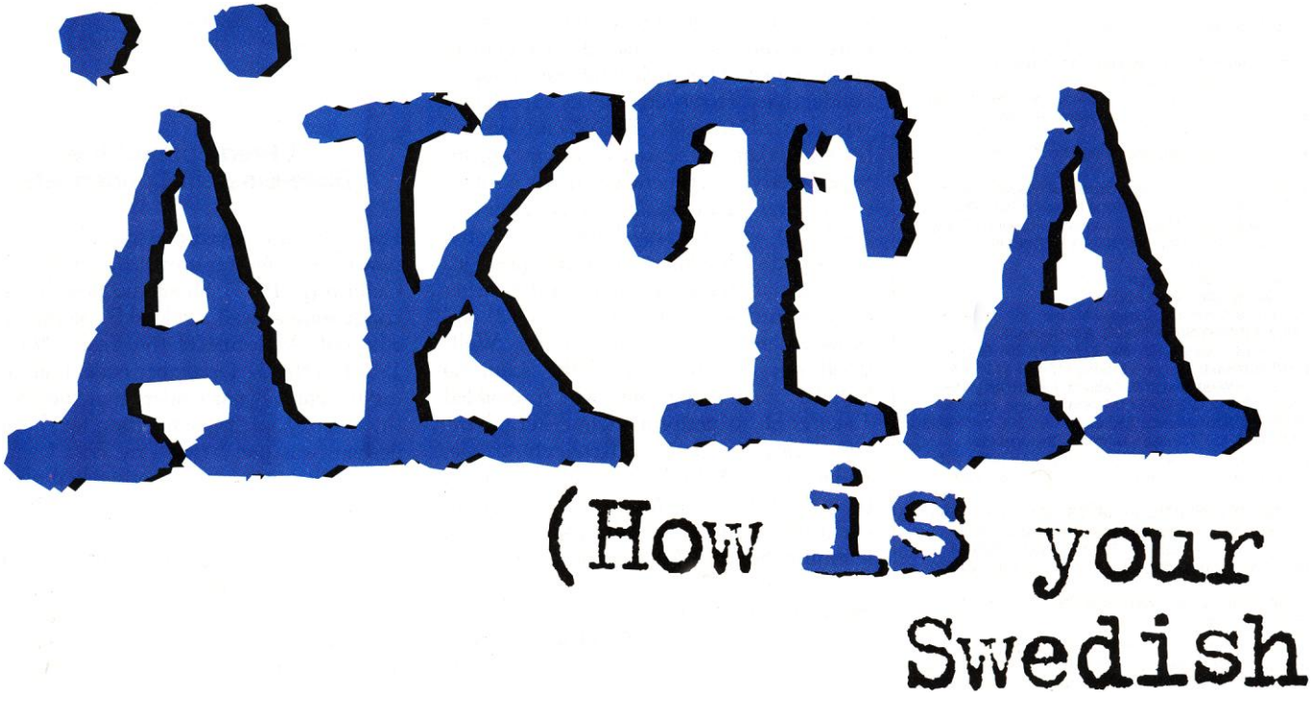
Air Quality in Mexico City

D. R. Blake and F. S. Rowland, in their report "Urban leakage of liquefied petroleum gas [LPG] and its impact on Mexico City air quality" (18 Aug., p. 953), state that LPG gas leakage and incomplete combustion of LPG are major precursors of ozone, the contaminant that most frequently exceeds Mexico air quality standards. Since 1992, the Instituto Mexicano del Petroleo has sampled Mexico City air and performed detailed chemical analysis of the volatile organic compounds (VOC) following the Environmental Protection Agency TO-14 protocol (*1*). In order to correlate the samples with ozone formation, a 3-hour sampling period was followed, as recommended by the U.S. National Ambient Air Quality Standards (*2*). The VOC sampling and analysis were carried out twice a year in different locations around the Mexico City metropolitan area (MCMA). From the earliest campaign (*3*) to the latest, in March 1995, propane and butane have been the most abundant compounds, constituting up to 30% of the VOC in the samples. These results made us aware of the impact that LPG has on the formation of ozone. The authorities have also expressed their concern about this problem.

It has been well established that the "reactivity" or relative ozone formation potential of individual VOCs differs (*4*). In general, alkanes and alcohols form less ozone than an equal mass of alkenes and carbonyls. More than 15 different reactivity scales have been proposed (*5*). The maximum incremental reactivity, developed by W. P. L. Carter (*6*) and chosen for regulatory application in California, has also been applied in Mexico City, with local adaptations. However, Carter (*7*) has suggested that this scale might not be applicable to Mexico City conditions, as it was designed for the relatively low ratios of VOC to nitrogen oxides (NO_x) typical of U.S. urban areas. In contrast, the mean VOC/NO_x ratio in MCMA is about four times that value (*8*).

The third most abundant compound found in our samples was toluene. We also found substantial amounts of ethylene, acetylene, and isopentanes—compounds mainly associated with solvent use and vehicular emissions (*9*). These compounds together constitute between 25 to 45% of the total VOC in the air. High concentrations of toluene have been measured during the morning traffic rush hours using remote sensing instruments. As the toluene concentration drops significantly at about 11:00 a.m., the absence of this compound in Blake and Rowland's samples may be attributed to their sampling protocol.

We also measured ambient carbonyl compounds, using the DNPH cartridge technique followed by high-performance liquid chromatography analysis (*10*). Formaldehyde, acetaldehyde, methylketone, benzaldehyde, *i*-propylmethylketone, and hexanal were the most significant carbonyls identified. Other major hydrocarbon components of the atmospheric mixture could be corre-



lated with the emissions of the approximately 3 million vehicles in the metropolitan area. In fact, the large amounts of ethylene and acetylene were used as fingerprints of car emissions, reflecting the present vehicular fleet in the MCMA. Incomplete gasoline combustion is also a common source of alkenes, the abundance of which is reported in Blake and Rowland's table 1. Fuel consumption in the MCMA also includes fuel oil, diesel oil, and gas oil (*11*). Blake and Rowland propose that LPG be reformulated to increase propane and decrease other components. As stated, the implementation of such a proposal should be accompanied by a major adjustment in LPG handling. Changing the composition to mostly propane would, with the current distribution and handling systems, lead to much more leakage and an associated increase in the risk of fires and explosions.

The domestic consumption of LPG in Mexico as end-use energy is equivalent to that of electricity. Even if the leakages in distribution and handling were controlled, the fugitive emissions from such a large number of residential sources might be difficult to control. Reducing VOCs from the LPG sector would not solve the ozone problem; a drastic reduction in hydrocarbon emissions would be needed across all sectors.

In our opinion, LPG contributes significantly to ozone formation but not to the extent that Blake and Rowland state. Further research on VOC reactivity under MCMA conditions is necessary before conclusive results are reached and to ensure which efforts are directed to the most effective control measures.

Francisco Guzmán
María E. Ruíz
Elizabeth Vega
Instituto Mexicano del Petroleo,
Eje Central Lázaro Cárdenas 152,
C.P. 07730 Mexico, D.F.

References

1. W. A. Wiberry, N. T. Murphy, R. M. Riggin, "Compendium of methods for the determination of toxic organic compounds in ambient air" (EPA-600-4-89-018, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1988).
2. B. J. Finlayson-Pitts and J. N. Pitts Jr., *Atmospheric Chemistry: Fundamentals and Experimental Techniques* (Wiley, New York, 1986).
3. S. M. E. Ruiz, K. Gerner, R. Seila, M. Barbiaux, paper presented at the 86th Annual Meeting of the Air and Waste Management Association, Denver, CO, 13 to 18 June 1993.
4. A. Russell, L. McNair, M. T. Odman, in preparation.
5. A. Russell *et al.*, *Science* **269**, 491 (1995).
6. W. P. L. Carter and R. Atkinson, *Environ. Sci. Technol.* **23**, 864 (1989).
7. W. P. L. Carter, paper presented at the Third International Technical Meeting on the Problem of Ozone in Metropolitan Zones, Oaxaca, Mexico, 1993.
8. S. Ruiz, K. Gerner, M. Y. Barbiaux, R. Seila, paper presented at the 86th Annual Meeting of the Air and Waste Management Association, Denver, CO, 13 to 18 June 1993.
9. R. L. Seila and W. A. Lonneman, paper presented at the meeting Measurement of Toxic and Related Air Pollutants, Durham, NC, May 1993.
10. S. M. E. Ruiz, paper presented at the First North American Conference and Exhibition, Toronto, Ontario, Canada, September 1994.
11. V. Samano, *Unidad de Control Opertiva* (Pemex-Refinacin, Mexico, 1995).

Response: We agree with Guzmán, Ruíz, and Vega that a drastic reduction in hydrocarbon emissions is needed across all sectors and that reducing volatile organic compounds from the LPG sector alone would not solve the Mexico City ozone problem. However, reductions in hydrocarbons from the transportation and industrial sectors alone would also not solve the ozone problem because of the significant presence of the hydrocarbons from LPG leakage. This point is particularly pertinent because the 1994 MARI joint report (*1*) from the Instituto Mexicano del Petroleo and Los Alamos National Laboratory lists 67 steps for improving Mexico City's air quality (*1*, vol. 5, pp. 7–8), none of them directed toward reducing LPG contributions. The only one that involves LPG is number 8, "convert public vehicles and delivery trucks to LP gas and install catalytic converters," which would tend, if anything, to increase the

LPG content of Mexico City air.

We are aware that the Instituto del Petroleo scientists had identified propane as a significant hydrocarbon in their earlier studies (reference 3 in their comment is reference 7 in our report) and that they had also qualitatively identified LPG as a source for propane (reference 9 in their comment). Nevertheless, as we discussed in our report, the 1994 MARI report (which cites both references 3 and 9 of their comment) states (*1*, vol. 3, p. 82), without any mention of LPG emissions, that

> [T]he major sources of VOCs in the atmosphere include exhaust and evaporative emissions from motor vehicles, evaporative emissions from chemical and petroleum industries. Recently, the importance of biogenic emissions (emissions from vegetation) has been pointed out as a major source of VOCs.

The most prominent LPG alkane in our data is propane, and there is no mention of measured propane concentrations in Mexico City anywhere in the five-volume report. The MARI report also provides an emissions inventory for VOCs in which "residential combustion" accounts for 331.2 metric tons per year out of a total of 624,954.3 metric tons per year (*1*, vol. 3, p. 88). We commented in our report that this 1994 MARI estimate of 331 metric tons from "residential combustion" seemed much too small for an area with annual sales exceeding 2 million tons and that LPG leakage needed to be included in the calculations. We agree that further research on the composition and reactivity of all of the hydrocarbons in Mexico City air is urgently needed if major progress is to be made toward solution of their serious air pollution problem.

The statement at the end of the third paragraph of their comment—"the absence of this compound [toluene] in Blake and Rowland's samples may be attributed to their sampling protocol"—is puzzling, because toluene was present in all of our samples and was so reported. Our table 1 reported the measured abundances of 25 hydrocarbons in four typical samples from our 1993 experiments, and toluene was reported as present in all of them. Indeed, when expressed in the units "ppbC" used in the MARI reports, toluene is the third most abundant hydrocarbon after methane and propane in the noontime Zocalo sample of table 1 in our report. However, the trend in our own data for toluene does not support the statement that "toluene concentration drops significantly at about 11:00 a.m." We have regularly observed more toluene at noon than at 6:00 a.m., as noted in our report. This difference could be the result of a more complicated diurnal dependence, as well as our use of samples, each collected in less than 1 minute rather than 3 hours. We prefer the near instantaneous collection procedure because we are greatly interested in the correlations among the individual hydrocarbon concentrations and believe the mixing of aliquots of air collected over several hours tends to complicate these signals.

As everyone recognizes, changing the composition of LPG gas toward higher total vapor pressure (for example, toward more propane) and lower chemical reactivity is not likely to be helpful with an overall system that already has a high rate of leakage. Our recommended reduction in the butene composition does not have this problem because the vapor pressures of the butanes and butenes are similar. If the composition of LPG sample M134 in table 3 of our report were hypothetically altered by substitution of *n*-butane for all of the C4 unsaturated compounds, then the total hydrocarbon reactivity would be reduced by about a factor of 2. For major overall hydrocarbon reduction in the LPG sector, however, the loss of unburned LPG at all stages of its handling must be addressed. This is obviously a difficult task because it involves about 5 million individual heating and cooking sources.

Donald R. Blake
F. Sherwood Rowland
Department of Chemistry,
University of California,
Irvine, CA 92717, USA

References and Notes

1. The Mexico City Air Quality Initiative (MARI) is described in a five-volume study produced by a collaboration between the Los Alamos National Laboratory and the Instituto Mexicano del Petroleo and published as *Los Alamos Rep. LA-12699* (1994).

■

Climate Change Consensus

I would like to reply to a letter by S. Fred Singer (2 Feb., p. 581). I also attended the Madrid meeting of the United Nations–sponsored Intergovernmental Panel on Climate Change (IPCC) in November 1995 and remember Singer's presence. As a nongovernmental organization (NGO) representative along with others in the environmental- and industry-sponsored lobbying groups, he was invited to attend and allowed to participate. Although he disputes the records of temperature change in his letter, I remember him asking only one question on ozone depletion and ultraviolet-B. He had full access to all meetings and on several occasions sought for and was given one-on-one meetings with several of the scientists present.

The IPCC summary is indeed a summary and does not include every piece of information that went into the full report. Much more supporting material, including most of the eclectic collection of facts highlighted