of workers (*17*) and has recently been proposed as a nonradiative model for aromatic hydrocarbon–induced carcinogenesis (*18*).

There is no experimental evidence relating chemiluminescence to any mechanism for carcinogenesis. However, cigarette smoke contains relatively stable carcinogens that may be metabolically activated. The spontaneous chemiluminescence observed indicates the potential for the production of electronically excited states within the lung over and above those metabolically produced excited states proposed by Anderson. The photon emission of cigarette smoke provides a minimum number for the excited state product molecules formed chemically.

Except for bioluminescence, in which an evolutionary selection has been made for chemiluminescent substrates that give high photon yields, most chemiluminescent reactions have very low photon yields. The detection of photon emission produced by these highly exergonic chemical reactions is in one sense fortuitous; nonradiative pathways and fluorescence quenching might have been so efficient as to make the luminescence, and therefore the presence of these reactions, undetectable. A possible interference in experiments on the promotion of carcinogenesis of tars by photoexcitation can be inferred from the self-absorption effect shown in Fig. 2a. A method for painting tars on the skins of mice and rabbits calls for a 50 percent solution (weight to volume) in acetone (*12*). This slurry produces a thick layer of tar so that incident light is absorbed by the outer layers of tar molecules—those not in contact with or absorbed by the skin. In view of the transient nature of the unstable radicals in cigarette smoke and their possible involvement in the promotion of carcinogenesis by activation of carcinogens already present, or as activated carcinogens themselves, it would appear that experiments attempting to relate cigarette smoke to carcinogenesis should also mimic the true physiological time exposures of the test organisms to the observed chemiluminescence [see also (*3*)].

Carcinogenic aromatic hydrocarbons are present in the air we breathe as the result of the burning of organic material, exclusive of tobacco. When tars and other latent carcinogenic molecules are already present in the lungs, the inhalation of chemiluminescent precursors in smoke from any source, as well as from tobacco, could result in a chemically mediated electronic excitation of these molecules, that is, a promotion of carcinogenesis. The long-lived nature of the chemiluminescence from smoke implies that, while smokers who inhale subject their lungs to relatively high intensities of chemiluminescence because of particulate retention, the chemiluminescent emission that occurs from exhaled smoke and the side-stream smoke subjects smokers and nonsmokers alike to a significant chemiluminescent dose.

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References and Notes

1. H. H. Seliger, in *Chemiluminescence and Bioluminescence*, M. J. Cormier, D. M. Hercules, J. Lee, Eds. (Plenum, New York, 1973), p. 461.
2. G. M. Barenboim, A. N. Domanskii, K. K. Turoverov, *Luminescence of Biopolymers and Cells* (Plenum, New York, 1969).
3. We are indebted to Dr. Richard Steele, Tulane University School of Medicine, and Prof. J. Stauff, University of Frankfurt am Main, for this chance remark during a conference on chemiluminescence in October 1972. We thank one of the reviewers for the reference to Stauff's report on his original observation [J. Stauff, G. Reske, I. Simo, *Z. Naturforsch. Teil C* **28**, 469 (1973)].
4. W. H. Biggley, E. Swift, R. J. Buchanan, H. H. Seliger, *J. Gen. Physiol.* **54**, 96 (1969).
5. H. H. Seliger and R. A. Morton, in *Photophysiology*, A. C. Giese, Ed. (Academic Press, New York, 1968), vol. 4, p. 274.
6. C. Lagercrantz and M. Yhland, *Acta Chem. Scand.* **17**, 1299 (1963).
7. H. H. Seliger and R. A. Morton, in *Photophysiology*, A. C. Geise, Ed. (Academic Press, New York, 1968), vol. 4, p. 290.
8. A detailed description of the spectral measurements and the kinetic measurements is in preparation.
9. H. H. Seliger, *J. Chem. Phys.* **40**, 3133 (1964).
10. Cigarettes were chosen from the 1972 Federal Trade Commission list of tar and nicotine content of 130 cigarette brands [reprinted in *Consumer Reports* (Orangeburg, N.Y., 1972), p. 471]. Tar and nicotine content of the cigarettes assayed for smoke chemiluminescence ranged over factors of 30 and 20, respectively.
11. H. H. Seliger, J. B. Buck, W. G. Fastie, W. D. McElroy, *Biol. Bull.* **127**, 159 (1964).
12. E. L. Wynder and D. Hoffmann, *Tobacco and Tobacco Smoke* (Academic Press, New York, 1967).
13. T. Takeshita and H. Ohe, *Sci. Pap. Cent. Res. Inst. No. 106* (Japan Monopoly Corp., 1964), p. 163.
14. H. H. Seliger and W. D. McElroy, *Science* **138**, 683 (1962).
15. W. Anderson, *Nature (Lond.)* **160**, 892 (1947).
16. W. Büngeler, *Klin. Wochenschr.* **16**, 1012 (1937); *Z. Krebsforsch.* **46**, 130 (1937); H. F. Blum, *Photodynamic Action and Diseases Caused by Light* (Reinhold, New York, 1941); M. A. O'Neal and A. C. Griffin, *Cancer Res.* **17**, 911 (1957); A. C. Griffin, R. E. Hakim, J. Knox, *J. Invest. Dermatol.* **31**, 289 (1958); F. Urbach, *ibid.* **32**, 373 (1959); B. A. Kihlman, *Exp. Cell Res.* **17**, 590 (1959); *Nature (Lond.)* **183**, 976 (1959); L. Santamaria, *Recent Contrib. Cancer Res. Italy* **1**, 167 (1960); ——— and G. Prino, in *Research Progress in Organic, Biological and Medical Chemistry*, U. Gallo and L. Santamaria, Eds. (Società Editoriale Farmaceutica, Milano, 1964), p. 259; L. Santamaria, G. G. Giordano, M. Alfice, F. Cascione, *Nature (Lond.)* **210**, 824 (1966); J. S. Bellin and G. Oster, in *Progress in Photobiology*, B. Christensen and B. Buchmann, Eds. (Elsevier, New York, 1961), p. 254; J. H. Epstein and W. L. Epstein, *J. Invest. Dermatol.* **39**, 455 (1962); J. H. Epstein, *J. Natl. Cancer Inst.* **34**, 741 (1965); ———, W. L. Epstein, T. Nakai, *ibid.* **38**, 19 (1967); J. D. Spikes in *Photophysiology*, A. C. Giese, Ed. (Academic Press, New York, 1968), vol. 3, chap. 2; H. E. Kubitschek, *Proc. Natl. Acad. Sci. U.S.A.* **55**, 269 (1966).
17. C. S. Foote and S. Wexler, *J. Am. Chem. Soc.* **86**, 3879 (1964); E. H. White, J. Wiecko, D. R. Roswell, *ibid.* **91**, 5194 (1969); E. H. White and C. C. Wei, *ibid.* **92**, 2167 (1970); E. H. White, E. Rapaport, H. H. Seliger, T. A. Hopkins, *Bioorg. Chem.* **1**, 92 (1971); A. A. Lamola, *Biochem. Biophys. Res. Commun.* **43**, 893 (1971).
18. N. P. Buu-Hoï and S. S. Sung, *Naturwissenschaften* **57**, 135 (1970).
19. We thank Prof. R. Ballentine for valuable discussions during the course of this work. Supported in part under AEC Division of Biology and Medicine contract AT(11-1)3277 and AEC Division of Environmental Biology contract AT(11-1)3278. Contribution 781 of McCollum-Pratt Institute and Department of Biology, Johns Hopkins University. J.P.H. is a National Institutes of Health predoctoral fellow.

29 March 1974

Microwave Hearing: Evidence for Thermoacoustic Auditory Stimulation by Pulsed Microwaves

Abstract. *Acoustic transients can be thermally generated in water by pulsed microwave energy. The peak pressure level of these transients, measured within the audible frequency band as a function of the microwave pulse parameters, is adequate to explain the "clicks" heard by people exposed to microwave radiation.*

When a person's head is illuminated with pulsed microwave energy, he can perceive "clicks" in synchrony with the individual microwave pulses (*1–3*). The pulses must be moderately intense (typically 0.5 to 5 watt/cm^2 at the surface of the head). However, they can be sufficiently brief (50 μsec or less) that the maximum increase in tissue temperature after each pulse is very small ($< 10^{-5}$ °C). This is the only unequivocal biological effect of microwave radiation that is not accompanied by or produced by observable tissue heating. Because of the current debate over possible effects on the central nervous system of low-power, radio-frequency radiation (*2*), it appears important to understand the underlying mechanisms for this phenomenon.

Electrophysiological experiments in cats have demonstrated the presence of

auditory evoked responses after exposure to pulsed microwave radiation identical to that which elicits "clicks" in humans (*3*). In the study reported here we show that this same radiation generates substantial (> 10 dyne/cm^2) sound transients in water, the major constituent of soft tissue. The peak pressure level of these transients, measured within the audible frequency band as a function of the microwave pulse parameters, is consistent with psychophysical observations of the loudness and threshold of this microwave "hearing" effect. We believe that the "clicks" are the perception, by bone conduction, of these thermally generated sound transients.

The conversion of electromagnetic to acoustic energy by the surface heating of a liquid is well known (*4*, *5*), for example, in connection with shock waves produced by a Q-switched laser (*6*). It is apparent that pulsed microwave energy is also capable of generating acoustic transients in absorbent materials. To illustrate this effect, assume that a uniform beam of electromagnetic energy of intensity I_0 (in watts per square centimeter) is directed at the surface of a fluid with an absorption coefficient α. The radiation intensity $I(x)$ at a distance x from the surface is given by

$$I(x) = I_0 T \exp(-\alpha x)$$

where T is the fraction of the incident energy transmitted into the fluid, the remaining energy being reflected. For 2450-Mhz microwave energy incident upon physiological saline (or upon soft tissue) at 37°C, T and $1/\alpha$ are approximately 0.4 and 1 cm, respectively (*7*). Assume that the beam is turned on at time $t = 0$ and off at time $t = \tau$. The fluid will expand as it is heated by this pulse and send out a pressure wave. The maximum velocity, u, of any small element of the fluid will be proportional both to the maximum rate of temperature rise ($\alpha T I_0 / C_p J \rho$, where C_p is the heat capacity at constant pressure, J is the mechanical equivalent of heat, and ρ is the fluid density) and to β, the volume coefficient of thermal expansion. Since the instantaneous sound pressure is directly proportional to the particle velocity, an approximate measure of the peak sound pressure produced by the absorbed energy is (*5*)

$$P_0 = \frac{c\beta I_0 T}{C_p J} \qquad (1)$$

where c is the velocity of sound in the fluid. A careful calculation must take into account the boundary conditions upon the fluid. It can be shown (*5*) that a pulse of electromagnetic energy of duration τ directed at a free (that is, unconstrained) fluid surface should produce both a positive and a negative pressure transient, of peak amplitude

$$P_{max} = \pm (P_0/2)[1 - \exp(-\alpha c \tau)] \qquad (2)$$

corresponding to the leading and trailing edges of the pulse, respectively. For incident energy of intensity 1 watt/cm^2 totally absorbed by water at 37°C, $(P_0/2)$ is approximately 6.5 dyne/cm^2.

We have verified these predictions, using a sensitive, electrically well-shielded hydrophone (an experimental model on loan from Chesapeake Instrument Corporation) and containers of various geometries filled with 0.15N KCl solution. A microwave generator (Applied Microwave Laboratories model PH-40) coupled to a standard gain horn (Waveline model 299) was used to produce pulses of 2450-Mhz radiation with a maximum peak intensity of approximately 10 watt/cm^2 and widths of 2 to 27 μsec. The microwave power density was measured with a probe (Narda model 8300). All measurements were carried out in an anechoic chamber lined with microwave-absorbent material.

A typical result showing positive and negative pressure transients with $P_{max} = 20$ dyne/cm^2 is given in Fig. 1. The solution, at 25°C, was contained in a cubic Lucite tank, 30 cm on a side. The 27-μsec pulse had a peak intensity of approximately 5.3 watt/cm^2 at the fluid surface. Most persons exposed to this radiation would hear a distinct "click." If 60 percent of the incident microwave power is assumed to be reflected by the water surface, Eq. 2 predicts a peak sound pressure of 10 dyne/cm^2; considering the relatively large errors inherent in microwave power measurements and the nonuniform surface heating produced by the diverging beam, the agreement between Fig. 1 and the theory is satisfactory. The shape of the transient resembles that predicted in (*5*) but is distorted by the presence of the Lucite wall. That the signal is due to thermal expansion of the water was confirmed by using a

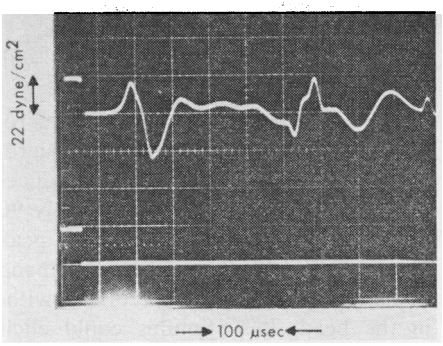

Fig. 1. Oscilloscope traces showing the acoustic transient (upper trace) produced by a 27-μsec, 2450-Mhz microwave pulse of intensity 5.3 watt/cm^2 (lower trace) incident upon 0.15N KCl solution at 25°C. The solution was contained in a cubic Lucite tank, 30 cm on a side. The latency between the microwave pulse and the first recorded transient is equal to the propagation time of sound from the front surface of the tank to the hydrophone; a reflection from the rear surface of the tank is also shown. This microwave pulse would elicit a "click" in most subjects.

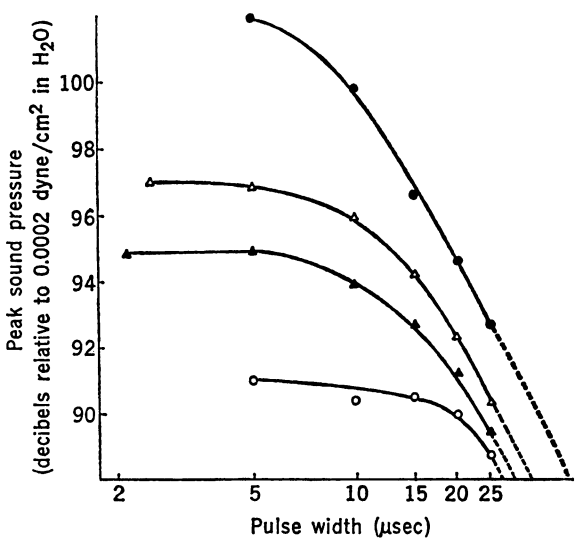

Fig. 2. The peak sound pressure of the microwave-generated acoustic transient, as a function of the microwave pulse width and filter bandwidth. Filter bandwidth: ●, 200 hertz to 60 khz; △, 200 hertz to 40 khz; ▲, 200 hertz to 30 khz; ○, 200 hertz to 20 khz. The 0.15N KCl solution was in a large rectangular expanded polystyrene tank, at 25°C. The sound pressures were increased by 2.9 db to simulate measurements at 37°C. The dotted lines indicate the function $P_0 \propto I_0$ (Eq. 1). This figure shows that, for short pulses, $P_0 \propto I_0 \tau$, in agreement with psychophysical observations of the microwave "hearing" effect. The microwave intensity was adjusted so that the incident energy density per pulse was 80 μj/cm^2, the threshold for microwave "hearing" in an average subject.

sample of distilled water and cooling the solution. Between 0° and 4°C the signal was inverted and at 4°C the signal vanished, in agreement with the temperature dependence of the thermal expansion coefficient of water. We have also observed in vitro acoustic transients produced by microwave pulses in such tissues as blood, muscle, and brain; similar transients have been observed in vitro in tissue after irradiation by a Q-switched laser (*8*).

The first reflection from the rear surface of the tank is shown in Fig. 1. Superficially, the initial transient and the following series of reflections (the "flutter echo") resemble a burst of white noise, which is exponentially damped with a time constant of about 3 msec as the sound energy is transferred to the walls of the container. The frequency spectrum of the burst depends upon the microwave pulse length and upon the geometry of the container; shortening the microwave pulse similarly shortens the initial transient but does not alter the decay time of the reflected pulses.

Using a variable band-pass filter (Kron-Hite), we have measured the band pressure levels of the acoustic transients that follow microwave pulses of different widths (Fig. 2). The solution at 25°C was contained in a large expanded polystyrene tank. The pressure levels were increased by 2.9 db to simulate measurements at 37°C. The incident total energy density per pulse, $I_0\tau$, was kept constant at 80 μj/cm^2. This is the approximate average threshold for microwave "hearing" in human subjects with normal hearing exposed to 2450-Mhz radiation, for pulses shorter than about 25 μsec repeated at a rate of three per second (*3*). For relatively long pulses, Fig. 2 shows that the P_{max} of the burst is directly proportional to I_0, consistent with Eq. 2. For shorter pulses, P_{max} depends upon $I_0\tau$ and upon the filter bandwidth. This is due to the exponential factor in Eq. 2 and to the broadened spectral distribution of the transients. Within the frequency band audible by bone conduction (200 hertz to 20 khz), the transition occurs at pulse widths of 20 to 25 μsec. In a psychophysical study Frey and Messenger showed, for pulsed 1245-Mhz radiation, that the loudness of the microwave "hearing" sensation depends only upon I_0 for pulse widths greater than about 30 μsec; for shorter pulses, their data show that the loudness is a function of the product, $I_0\tau$ (*1*). These results are consistent with our observations.

We observe that in water a microwave pulse, at the threshold for microwave "hearing" in humans, produces pressure transients of approximately 90 db relative to 0.0002-dyne/cm^2 peak amplitude within the frequency band 200 hertz to 20 khz. If occurring within the head, this stimulus could elicit a "click" when some of the sound energy is coupled into the skull. Neither the duration of the flutter echo produced inside the head by a microwave pulse nor the threshold for perception of this unusual stimulus is known. However, 90 db is above the expected threshold (~ 80 db) for perception, by bone conduction, of millisecond bursts of white noise incident upon a subject's skull in water (*9*). It is therefore reasonable to believe that these thermally induced transients elicit the microwave "hearing" sensations in humans.

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References and Notes

1. A. H. Frey and R. Messenger, Jr., *Science* **181**, 356 (1973); A. H. Frey, *J. Appl. Physiol.* **17**, 689 (1962).
2. A. H. Frey, *Inst. Elec. Electron. Eng. Trans. Microwave Theory Tech.* **MTT-19**, 153 (1971).
3. A. W. Guy, E. M. Taylor, B. Ashleman, J. C. Lin, *Inst. Elec. Electron. Eng. Int. Symp. Digest Tech. Pap. G-MTT* (1973), p. 321; A. W. Guy, C. K. Chou, J. C. Lin, D. Christensen, *Proc. N.Y. Acad. Sci.*, in press.
4. R. M. White, *J. Appl. Phys.* **34**, 3559 (1963).
5. L. S. Gournay, *J. Acoust. Soc. Am.* **40**, 1322 (1966). The quantity β is the volume coefficient of thermal expansion, not the linear coefficient as stated by Gournay. This can be demonstrated by an independent derivation of the fundamental differential equation for thermally driven pressure waves in fluids, equation 9 of this reference, from the first-order acoustic equations for a fluid [see F. A. Firestone, in the *American Institute of Physics Handbook*, D. E. Gray, Ed. (McGraw-Hill, New York, 1957), p. 3-33.
6. C. L. Hu, *J. Acoust. Soc. Am.* **46**, 728 (1969).
7. H. N. Kritikos and H. P. Schwan, *Inst. Elec. Electron. Eng. Trans. Biomed. Eng.* **BME-19**, 53 (1972).
8. S. F. Cleary and P. E. Hamrick, *J. Acoust. Soc. Am.* **46**, 1037 (1969).
9. W. R. Thurlow and R. Bowman, *ibid.* **29**, 281 (1957); P. M. Hamilton, *ibid.*, p. 792.
10. We thank the Chesapeake Instrument Corporation of Shadyside, Maryland, for the generous loan of the hydrophone used in this work. Supported by the Bureau of Medicine and Surgery Work Unit No. MF51.524.-015.0018BE7X. The opinions or assertions contained herein are the private ones of the authors and are not to be construed as official or reflecting the views of the Navy Department or the naval service at large.

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Surface Electronic Properties of Tungsten, Tungsten Carbide, and Platinum

Abstract. *The local electronic structures of the surface regions of tungsten, tungsten carbide, and platinum have been compared. Contrary to the hypothesis that the platinum-like catalytic activity of tungsten carbide results from the contribution of carbon valence electrons to the 5d band of tungsten, the width of the unfilled portion of the d band increases on going from tungsten to tungsten carbide.*

It has been shown (*1*, *2*) that transition metal carbides have many of the desirable catalytic properties of "noble" metals (such as Pt and Pd) with respect to hydrogen oxidation and hydrogenolysis reactions, but there is no detailed understanding of this phenomenon. Levy and Boudart (*2*) have proposed that the increased catalytic activity of WC over W is due to the donation of electrons by carbon to the W 5*d* band, resulting in an electronic structure similar to that of Pt. In this report we test their hypothesis by directly comparing the density of unfilled electronic states in the conduction bands of W, WC, and Pt by soft x-ray appearance potential spectroscopy (SXAPS) (*3*, *4*). The measurements are sensitive to the catalytically active outermost few atomic layers. Contrary to the hypothesis of Levy and Boudart, we find that the width of the unoccupied portion of the 5*d* band of W actually increases on going from W to WC. As expected, we find that the unoccupied portion of the 5*d* band of Pt is quite narrow, indicating that the band is almost completely filled.

In SXAPS one monitors the total x-ray emission from a sample bombarded with electrons as a function of the energy of the incident electron beam. The resulting curve exhibits distinct structure corresponding to the excitation probabilities for core level electrons superimposed on a smoothly increasing bremsstrahlung background. The background is suppressed relative to the excitation structure by differentiating the curve with respect to energy. Neglecting the finite lifetime of