Nitrogen: Formation by Photooxidation of Ethylene in the Presence of Its Oxides

Abstract. *The apparent lack of nitrogen balance for the photooxidation systems containing olefin and nitrogen oxides can be explained by evidence for the production of molecular nitrogen; molecular nitrogen was identified by gas chromatography and mass spectrometry.*

Models for photooxidation mixtures of hydrocarbons and nitrogen oxides have led to better understanding of the processes in photochemical-type air pollution. However, no adequate proof of a nitrogen balance exists. Investigators apparently have assumed that the oxides of nitrogen either have been adsorbed on the reaction vessel or have combined with carbon fragments to form polymers on the walls of the vessel.

In the photooxidation of ethylene in the presence of oxides of nitrogen, the nitrogen balance cannot be explained by either adsorption or by formation of polymers. Altshuller and Cohen (*1*) accounted for 70 to 100 percent of the available carbon as formaldehyde and carbon monoxide under various conditions when ethylene was photooxidized in the presence of nitrogen oxides and ultraviolet light. No peroxyacylnitrate-type compound was observed, and only very little methyl nitrate could be detected. Tests were performed for adsorption and permeation of nitric oxide and nitrogen dioxide through the vessel. The combined rates were much lower than the photooxidation rate. Since most of the carbon atoms can be accounted for, a highly exotic polymer of carbon and nitrogen would have to be postulated to explain the anomaly of the nitrogen balance. The existence of such a polymer with a large ratio of nitrogen to carbon is unlikely.

Ethylene (20 parts per million by volume) was photooxidized in the presence of nitrogen dioxide (9 ppm) under dynamic flow conditions in a 22-liter Pyrex flask reactor. The flow rate of 500 cm^3/min gave a residence time of 44 minutes for the reactants. The simulated atmosphere was composed of 20 percent oxygen and 80 percent helium. The light source consisted of two parallel banks of General Electric F 42 T6 BL blacklights with an energy maximum at 3660 Å. The light intensity was measured by NO_2 photolysis. The first-order dissociation constant (K_d) for NO_2 in a nitrogen atmosphere was approximately 0.4 min^{-1}. Colorimetric analyses for NO_2 were made throughout the irradiations; the modified Griess reagent was used (*2*). Ethylene was monitored by a gas chromatograph equipped with a silica-gel column. Nitrogen was detected in parts per million by volume by vapor-phase chromatography on two 1.8-m glass columns 13 mm in diameter, packed with 5A molecular sieves. The helium-type ionization detector operated in the multiplicative range.

The nitrogen background before irradiation was 4.5 ppm at steady state. After ultraviolet irradiation, the nitrogen concentration increased to 5.1 ppm. This concentration accounts for approximately 80 to 90 percent of the nitrogen dioxide consumed under the conditions of reaction.

Higher concentrations of ethylene (100 ppm) and nitrogen dioxide (30 ppm) were photolyzed in static tests made with Teflon FEP or Saran-coated Mylar bags. In each case, the infrared spectra (cell with 10-m path length) could account for only a very small percentage of the nitrogen compounds. Bands that could be ascribed to nitrous oxide and methyl nitrate were in evidence. In addition, the infrared spectra indicated the presence of peroxyacylnitrate-type compound. The total nitrogen in all the compounds was far less than the molar amount of nitrogen dioxide originally used.

To confirm the evidence for formation of molecular nitrogen, further photooxidations were performed with ethylene and $^{15}NO_2$ in the diluent mixture of helium and oxygen. The dark control and the irradiated sample were both contained in high-vacuum mass spectrometer bulbs. All condensibles were trapped out at liquid-nitrogen temperature before introduction of the sample to the Bendix time-of-flight mass spectrometer. The instrument was calibrated with known concentrations of $^{15}N_2$. Some measurement of its sensitivity can be shown by its ability to see the mass-30 peak in an air sample due to the isotopic abundance of ^{15}N.

A mixture of ethylene and $^{15}NO_2$ (17.5 ppm and 24.6 ppm, respectively) was photooxidized sufficiently to convert 9.1 ppm of $^{15}NO_2$ to products. Approximately 86 percent of the nitrogen inbalance was accounted for as molecular $^{15}N_2$.

Molecular nitrogen was not found when NO_2 was irradiated in the absence of ethylene. This observation is compatible with earlier work (*3*) in which it was shown that all of the oxides of nitrogen can be accounted for as nitric oxide and nitrogen dioxide.

These data suggest that much of the nitrogen initially present as oxides was ultimately converted to molecular nitrogen. Altshuller and Cohen have shown that an excess of nitric oxide inhibits the photooxidation rate of ethylene. They suggest a chain-terminating step such as

$$CH_3 + NO \rightarrow CH_3NO$$

If the alkyl free-radical (R) does indeed react to form the corresponding nitroso compound, then a mechanism such as that proposed by Brown (*4*) and discussed by Strausz and Gunning (*5*) seems feasible.

$$\begin{gathered} R + 3NO \rightarrow RN_2ONO_2 \\ RN_2ONO_2 \rightarrow R + N_2 + NO_3 \\ NO_3 + NO \rightarrow 2NO_2 \end{gathered}$$

The net results of these reactions is

$$4NO \rightarrow N_2 + 2NO_2$$

The beauty of this mechanism is that the alkyl radical reappears and that nitric oxide is consumed.

The various steps in this mechanism may not be important with all hydrocarbons and at all concentrations. Tuesday (*6*) obtained a satisfactory nitrogen balance in irradiation of a mixture of *trans*-2-butene and nitrogen oxide. However, even this system shows a satisfactory balance only when *trans*-2-butene is in excess of nitrogen oxide.

The presence of nitrous oxide (4.54-μ band) presumably indicates the following sequence of reactions:

$$\begin{gathered} CH_3O + NO \rightarrow CH_2O + HNO \\ 2HNO \rightarrow (HNO)_2 \\ (HNO)_2 \rightarrow N_2O + H_2O \end{gathered}$$

The presence of such a small amount of N_2O should be expected, for other investigators have shown that the presence of molecular oxygen decreases its yield (*7*).

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References

1. A. P. Altshuller and I. R. Cohen, *Intern. J. Air Water Pollution* **8**, 611 (1964).
2. B. E. Saltzman, *Anal. Chem.* **26**, 1949 (1954).
3. J. J. Bufalini and E. R. Stephens, *Intern. J. Air Water Pollution* **9**, 123 (1965).
4. J. F. Brown, *J. Am. Chem. Soc.* **79**, 2480 (1957).
5. O. P. Strausz and H. E. Gunning, *Can. J. Chem.* **41**, 1207 (1963).
6. C. S. Tuesday, in *Chemical Reaction in the Lower and Upper Atmosphere*, R. D. Cadle, Ed. (Interscience, New York, 1961), pp. 1–49.

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Evoked Visual Potentials and Human Color Vision

Abstract. *The waveform of the evoked visual potential is color specific. This specificity is absent in a color-deficient observer.*

There is a long history of attempts to develop objective means for gauging individual differences in human color vision. Such reflexes as the pupillary and the optokinetic have been tried with no genuine success. More recently, the single-flash electroretinogram has been used but with only a little more efficiency.

Some laboratories are now studying evoked occipital potentials. General agreement on two important facts is emerging. (i) The evoked occipitogram reflects primarily foveal luminosity characteristics (*1*); and (ii) because of this foveal bias, the occipitogram may bear a closer relationship to visual psychophysics than any other electrophysiological measure yet obtained in man (*2*).

We give here the results obtained from three highly trained observers (ourselves). Our data have revealed an important color and individual specificity in the waveform of the evoked response which has not been reported (*3*). This report covers the following kinds of light: xenon white, and colors of wavelengths (in nanometers) of 680, 575, 520, and 400, obtained with narrow-band interference filters. The colors, a deep red, a yellow-green of minimum saturation, a rather full green, and a blue-violet, were chosen with some care.

One point must be made about method—studies of visually evoked-potentials should be done with Ganzfeld or Maxwellian-view stimulation. With the first method the whole eye is filled uniformly with light, and with the second the image of the source itself is placed within the pupil of the subject's eye. We have used the Maxwellian-view technique. By no other method have we been able to obtain the reliability which we can now report.

We use a 500-watt xenon lamp as our source. A rotating aperture disc exposes the light for approximately 0.01 second. The waveform of the flash is flat-topped and rises and falls gradually. The stimulus duration is very much longer than that more typically obtained with the widely used electrical discharge lamps (for example, the Grass PS2 has a flash lasting 10 μsec), and this longer flash duration could be an important factor in our results. However, as with discharge lamps, we are also using a stimulus waveform which has both on-and-off characteristics, and we are aware that our results may be further complicated by this fact (*4*). Although controlling the light flashes mechanically sacrifices some of the exactness obtainable electronically, it has one important ancillary advantage. There is no audible discharge click synchronous with the flash. Our subjects hear only a low steady rumble. Evoked auditory potentials are very large, and it is well known that they can contaminate the visual response. Our method avoids such intersensory influences.

The disc cuts the light beam at a focus and the beam then passes through a camera shutter. This shutter is closed between test runs to allow for control of the observer's dark- and light-adaptation. The beam is collimated

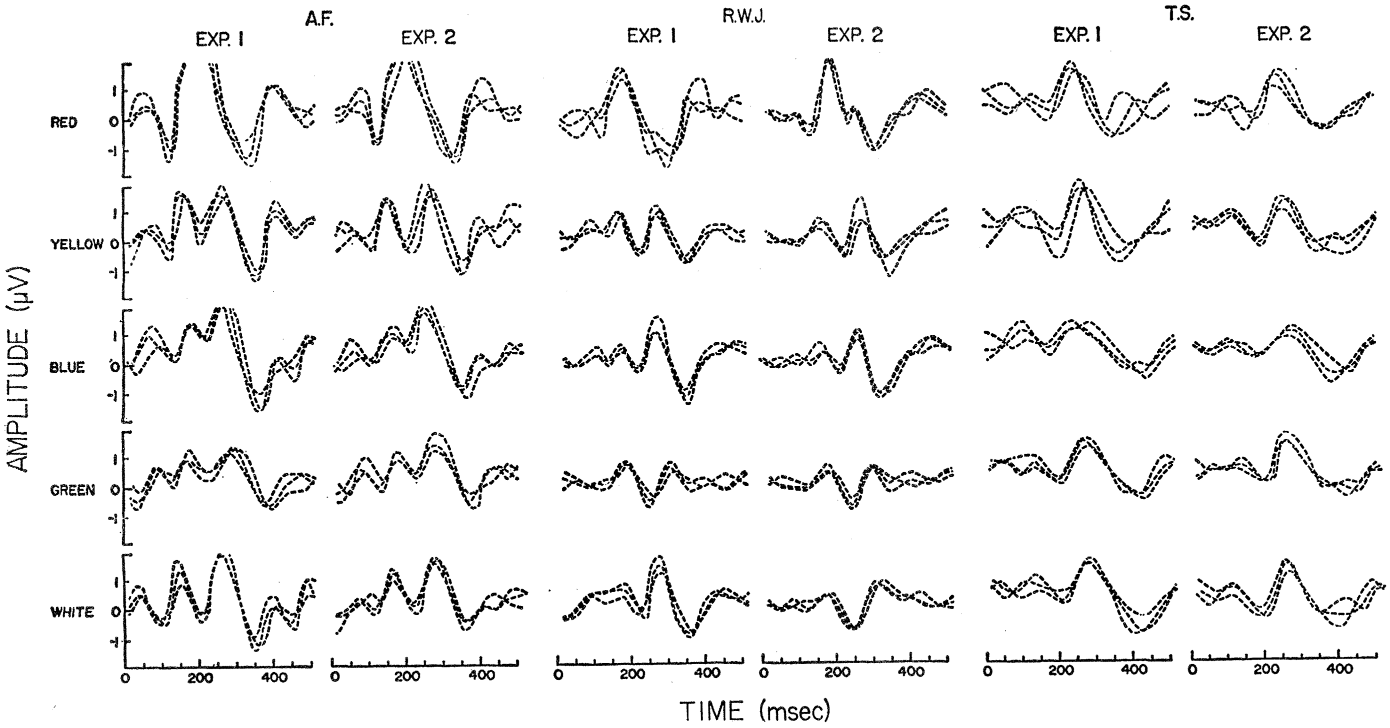

Fig. 1. The chromatic evoked occipitogram in man. A.F. and R.W.J. are color-normal observers, and T.S. is a deutan observer. In experiment 2 observations on R.W.J. were taken with the electrodes at 5 mm separation.