revealed no systematic or significant growth as a function of trial position at any electrode site. When the averages were computed on the basis of reaction time (Fig. 2, right), however, the late CNV wave showed a significant inverse relationship to reaction time (*14*), while the early wave was not related to reaction time.

We believe these data delineate and confirm the functional separation of two component processes in the CNV, one a negative afterwave associated with the warning stimulus and the second identified with the readiness potential. We have been able to distinguish these elements by minimizing the temporal overlap between the two at an interstimulus interval of 4 seconds. Additional processes may well become involved at shorter interstimulus intervals or under different conditions. However, the two waves described here would be sufficient, when temporally overlapped and coalesced, to form CNV's resembling those often obtained at short interstimulus intervals. Any such mixture of the two negative waves would mutually dilute individual relationships between the respective waves and the experimental variables associated with each, for instance, the relationship we observed between reaction time and amplitude of the late CNV wave.

Our results suggest that the more important effects of the pairing of stimuli lie in the temporal conjunction of these two waves. A connection or contingency between the stimuli may not be directly or uniquely responsible for the production of the individual negative variations we have studied. Frontal waves having similar features were elicited by the tone whether or not it was paired with a subsequent imperative stimulus. These observations indicate that pairing a given stimulus with another may be but one manipulation that causes a stimulus to elicit a negative afterwave. Other manipulations might include requiring close attention to the stimulus (as in the unpaired tone condition of the present study), raising stimulus intensity (*4*), or assigning to it some experimental importance by requiring a discrimination or by making it rare or novel (*15, 16*). Others (*4, 5, 10*) have speculated that the effect common to these manipulations is an orienting response—an interpretation we cannot easily reconcile with our finding that the negative afterwave grows in amplitude over repeated trials.

Likewise, the late CNV wave appears not to be strictly contingent on the pairing of stimuli, in that it reflects a process of response preparation rather than stimulus anticipation. If, as we believe, the late CNV wave is primarily a readiness potential, then the study of the readiness potential can be extended beyond the scope of repetitive stereotyped movements. In addition to the present variable of response speed, it may be possible to examine the readiness potential within the context of heretofore inaccessible variables, such as the degree to which the eventual response is specified and its susceptibility to distraction by competing timed mental or motor processes.

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11. Statistical tests were based, in the case of the early wave, on the single most negative point within 400 to 1000 msec after the tone burst. The late wave was measured as the average amplitude over the last 500 msec preceding the flash or, in the case of the uncued responses, before the response. Analyses of variance revealed that the midline differences were significant for the early wave during the unpaired tones (F = 13.18; d.f. = 2, 26; $P < .005$) and both blocks of paired stimuli (F = 39.11; d.f. = 2, 26; $P < .001$; and F = 73.70; d.f. = 2, 26; $P < .001$). The midline differences were also significant for the late wave during the uncued responses (F = 8.18; d.f. = 2, 26; $P < .005$) and both blocks of paired stimuli (F = 9.22; d.f. = 2, 26; $P < 001$; and F = 8.39; d.f. = 2, 26; $P < .005$).
12. The interaction of responding hand with lateral electrode site was significant for the late wave in the uncued response condition (F = 18.59; d.f. = 1, 13; $P < .001$) and both blocks of paired stimuli (F = 10.40; d.f. = 1, 13; $P < .01$; and F = 5.84; d.f. = 1, 13; $P < .05$). The late CNV wave averaged 5.3 μv for the contralateral hemisphere versus 4.1 μv for the ipsilateral hemisphere during the first block of paired stimuli, 4.4 μv versus 3.4 μv during the second block of paired stimuli, and 2.8 μv versus 1.4 μv for the readiness potential. Over all 14 subjects the contralateral-ipsilateral differences in the readiness potential correlated significantly with differences in the late CNV wave during the second block of paired stimuli (r = +.56, $P < .05$).
13. The early wave differed significantly in amplitude between the first and last 20 trials for both blocks of paired stimuli, measured at Fz (F = 7.56; d.f. = 1, 13; $P < .025$; and F = 7.29; d.f. = 1, 13; $P < .025$).
14. Differences in the late wave at Cz were significant over the three reaction time categories, measured during the second block of paired stimuli (F = 4.97; d.f. = 2, 26; $P < .025$). The late CNV waves from the bilateral (C3 and C4) electrode sites, as plotted in Fig. 2, had the following values during the second block of paired stimuli: for the fast reaction times the contralateral value averaged 6.4 μv versus 4.9 μv from the ipsilateral electrode, 3.8 μv versus 3.0 μv for the middle reaction times, and 2.5 μv versus 2.1 μv for the slow reaction times.
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16. Prior work in our laboratory (J. W. Rohrbaugh, K. Syndulko, D. B. Lindsley, in preparation), as well as studies by Loveless and Sanford (*4, 5*) and Weerts and Lang (*10*), has established that the early CNV wave cannot be attributed solely to the fact that the warning stimulus required a discrimination. In our prior work 12 subjects each received four reaction time conditions given in the same order. In the first three of these conditions (using simple, go or no-go, and choice reaction time) the warning stimulus was a nondiscriminative tone of the same pitch on every trial. The fourth condition was similar to the one used here, with a discriminative tone of either 1000 or 1500 hertz. In all conditions the warning stimulus elicited a negative afterwave that peaked at about 8 μv (at Cz) and differed by no more than 1 μv from one condition to another.
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Photochemical Smog Systems: Heterogeneous Decay of Ozone

Fox *et al.* (*1*) describe the results of two experiments from which they conclude that "dilution as opposed to static experimental conditions may prove to be more important if smog chamber data are to be used as guides in developing certain future control strategies." Although the above suggestion may be correct, the evidence presented by Fox *et al.* (*1*) is incomplete in at least one serious aspect. At the low dilution rates associated with their reported smog chamber experiments, the heterogeneous decay of O_3 (*2, 3*) could well be the dominant mechanism by which O_3 is lost from the gas phase. Since Fox *et al.* neither mention the material from which the chamber is made nor state the results of pertinent auxiliary experiments, the reader has no way of assessing the influence of the mechanism of heterogeneous decomposition upon the concentration of O_3.

The following approximate calculation, involving the model of a well-mixed chemical reaction with flow, demonstrates my main concern. In this case the mass balance for O_3 can be expressed as

$$V\frac{dc}{dt} = qc_{in} - qc + \sum_i \text{sources} - \sum_j \text{sinks}$$

where V is the chamber volume, c is the O_3 concentration in the chamber taken to be uniform throughout, t is time, q is the dilution flow rate, and c_{in} is the O_3 concentration in the incoming stream. The value of c_{in} was probably near zero in each of the two experiments reported by Fox *et al.* Some of the sources and sinks involve homogeneous mechanisms, the rates of which no doubt vary with time. One sink for O_3, involving its heterogeneous decomposition on the chamber surface, can be represented by kAc, where k is the rate constant and A is the chamber surface area. The dimensionless quantity kA/q indicates the relative importance of heterogeneous decomposition to dilution in reducing the concentration of O_3 in the chamber. The value of A is estimated to be at least $6 \times (156)^{2/3}$ or 174 m^2. The value of k depends upon the wall material and its history, and may vary with temperature and relative humidity. Typical values of k range from 10^{-2} to about 1 m/hour (*2*). Indicated values of q were 8.9 and 14.8 m^3/hour (*1*). Consequently, values of kA/q are estimated to lie between about 0.2 and 20. Since the O_3 concentrations in the dilution and static chambers in the experiments of Fox *et al.* differed at most by about 30 percent, the values of kA/q should certainly be less than 0.1 before qualitative conclusions can be correctly inferred.

As shown in figure 1 of Fox *et al.*, when significant differences in O_3 concentrations existed between the two chambers, the blue chamber always exhibited lower values of O_3 concentrations. Changes in the concentration of such species as water vapor might easily have reduced the value of k in the blue dilution chamber during the 26 August 1974 test, thus accounting for the slightly higher concentrations of O_3 in the blue dilution chamber from 9:30 a.m. to 11:30 a.m.

It may be that the values of k for each chamber are either always equal or negligible; however, unless the heterogeneous mechanism associated with the decay of O_3 in each chamber is carefully considered, the conclusion of Fox *et al.* cannot be taken seriously. It is my hope that Fox *et al.* will take this opportunity to possibly strengthen the basis upon which their conclusion now rests.

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Shair suggests that heterogeneous decay of O_3 could be the dominant mechanism in studies that we recently described (*1*), thus invalidating our conclusions.

The reaction chamber surfaces are 5-mil fluorinated ethylene-propylene (FEP) Teflon (< 1 percent of the surface is aluminum). For this Teflon surface, the highest heterogeneous decomposition rate constant (k) for O_3 ever observed in the chambers was 7×10^{-4} min^{-1} (or 3×10^{-2} m/hour in Shair's notation), a 16.5-hour half-life. Shair suggests that the values of k may have been significant in magnitude and sufficiently different for the dilution (Red, 7 October) and the static (Blue, 7 October) sides to account for the observed effect. Although the mass balance as stated by Shair is correct, his analysis of the effect of the heterogeneous term overlooks the fact that O_3 is in photostationary equilibrium (PSS) with NO and NO_2, as well as with the heterogeneous loss. If a complete mass balance for O_3 is carried out and the PSS assumptions are applied, the following results are obtained:

$$[O_3] = \frac{k_1[NO_2]}{k_2[NO] + k_3[NO_2] + k_4[HC] + k}$$

[Note: NO measurements below 0.025 parts per million (ppm) were subject to a positive 50 percent interference (*2*).] The terms in the denominator express the relative importance of the O_3 sinks. Typical pseudo first-order values for this series of terms near the end of the 7 October experiment are as follows (in units of reciprocal minutes): 0.292, assuming NO = 0.012 ppm; 9.2×10^{-4}, assuming NO_2 = 0.2 ppm; 7.2×10^{-5}, assuming HC = 0.28 ppm; and the heterogeneous loss $k = 7 \times 10^{-4}$. The relative importance of these O_3 sinks is 99.4, 0.31, 0.02, and 0.24 percent, respectively.

Surprisingly, if one proceeds as Shair suggests, the analysis given in (*1*) is still valid. The worst case assumptions would be: (i) dilution eliminated any heterogeneous loss in the diluted side, and (ii) the highest heterogeneous loss rate ever observed was in effect in the static side. These conditions imply that no correction for heterogeneous loss to the observed O_3 is necessary in the diluted side, and, if PSS is ignored, the highest positive correction to O_3 may be applied in the static side.

An iterative equation

$$C_n^P = C_{n-1}^P + (C_n^O - C_{n-1}^O) + C_n^O \frac{kA}{V}(\Delta t)$$

where A is the chamber surface area and V is the chamber volume, was used to correct the observed O_3 (C^O) for heterogeneous loss for the 7 October experiment. A constant time interval Δt was used to obtain the predicted O_3 (C^P). At 1700 hours, C^P in the static side was 0.080 ppm (C^O = 0.072 ppm) compared with 0.096 ppm in the diluted side. Thus, even under worst case assumptions, the conclusion in (*1*) still holds. A detailed report of chamber performance including O_3 decay studies is presented elsewhere (*2*).

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