junction with predetermined fade rate constants to calculate the past temperature exposure.

To facilitate the use of TLD's for measuring temperature exposure, we have constructed "TLD temperature tags" that contain sufficient TLD materials to allow replicate determinations and thus minimize analytical error. These tags were developed for use in environmental research (3), but they can readily be applied to numerous other research and industrial activities. Tag construction and fade characteristics will vary, depending on the specific application and the TLD phosphor used; however, a description of the tags that we have used for monitoring average environmental water temperatures and the thermal exposure of free-swimming fish will illustrate the conceptual and procedural methods.

The TLD phosphor used for this application was $CaSO_4$:Mn incorporated in a Teflon matrix. We constructed the tags by sealing 12 $CaSO_4$:Mn TLD's (microrods containing 8 percent phosphor by weight) in a length of stainless steel tubing. This procedure produces a small, durable tag (30 mm long and 3 mm in outside diameter), at a cost of $1.30 per tag. All tags were simultaneously exposed to 250 roentgens (^{60}Co) at room temperature and subsequently stored at 26.4°C for 240 hours to empty undesirable shallow traps. The standard error of the mean TL value of any tag (12 individual readings) was 3 percent at the 95 percent confidence level.

We determined fade characteristics by monitoring the fade response at isothermal conditions (Fig. 1). For these tags, isothermal fade between 10° and 26°C approximated a hyperbolic function of the form

$$\frac{1}{S} = \frac{1}{S_0} + m_T t$$

where S is the TL signal at time t, S_0 is the initial TL signal, and m_T is the rate of change in $1/S$. In this case, the uniform slope m_T was used as the temperature-dependent fade rate and it increased rapidly with increasing temperature; m_T approximately doubled for every 5°C rise. Since fade was retarded at low temperature, the tags were kept at temperatures below -25°C to preserve the stored TL signal prior to their use and analysis.

The increased sensitivity of $CaSO_4$:Mn tags at higher temperatures is advantageous for certain applications, but it can cause the calculated average temperature to be greater than the true average temperature exposure. This problem arises when the tags are used in varying temperature conditions, since exposure to a fluctuating temperature produces more fade than a uniform exposure to the same average temperature. The total difference depends on the temperature range and the apportionment of time between temperatures. Figure 2 illustrates the expected difference in accumulated fade due to exposure to a variable (point A) and a uniform (point B) temperature of 15°C. For this extreme case, where time is equally divided between two temperatures, the calculated average temperature is only 10 percent (1.5°C) greater than the true average temperature exposure. Closer agreement is expected for less extreme cases.

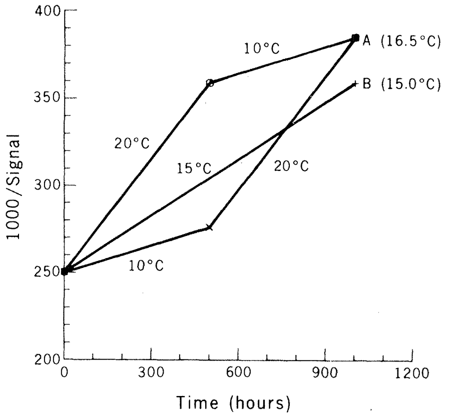

Fig. 2. A hypothetical example illustrating a difference in accumulated fade due to a fluctuating (A) and a uniform (B) average temperature exposure of 15°C. The anticipated TL signals were calculated on the basis of previously determined fade rates for the temperatures indicated. The calculated average temperatures (based on the final TL signal) are given in parentheses.

If more than one type of TLD phosphor is used in each tag, it would be possible to more accurately define average temperature in a manner similar to that of qualitatively measuring radiation by utilizing the different energy dependence of two phosphors (4). One can obtain a wide range of fade rates by selecting phosphors that are characterized by different trapping depths. It is also possible to adjust the fade properties of individual phosphors by using various preconditioning treatments (5). Ideally, fade rate should remain uniform at a given temperature and be matched to the time-temperature conditions of interest. Further details concerning the use of TLD's for measuring temperature exposure are reported elsewhere (6).

Since TLD phosphors (i) are easy to use, (ii) are small, (iii) are relatively inexpensive, and (iv) have a wide range of fade rates, they provide a valuable research tool that can be used to measure temperature exposures under a variety of conditions.

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Hydroxyl Radical Reactivity with Diethylhydroxylamine

Abstract. *Diethylhydroxylamine (DEHA) reacts with gas-phase hydroxyl radicals on every third collision, whereas the corresponding reaction in aqueous solution is considerably slower. The high gas-phase reactivity explains the predicted inhibitory effect of DEHA in atmospheric smog processes. Results from the studies in the aqueous phase are helpful in predicting the mechanism of the reaction of DEHA with hydroxyl radicals.*

Maugh (1) recently discussed the proposal of Heicklen and his co-workers (2) to use *N,N*-diethylhydroxylamine (DEHA), $(C_2H_5)_2NOH$, as a radical scavenger in urban airsheds to inhibit smog chemistry. In order to learn how and why DEHA might be effective, we have initiated a study of the reactivity of DEHA with radical species known to be chemically significant in atmospheric pollution reactions.

The hydroxyl radical (OH) is now regarded as being very important in smog chemistry. Pitts and his co-workers (3) have demonstrated that the rate of disappearance of alkanes, alkenes, and aromatic hydrocarbons in a synthetic polluted air mixture in their environmental chamber correlates with the known reactivity of these organic compounds with OH radicals. They have also used this method to estimate the reactivity of other organic pollutants with OH (*4*).

In our study we have used the techniques of gas-phase (*5*) and aqueous pulse radiolysis (*6*) with high-energy electrons to rapidly generate a high initial yield of OH in the presence of varying concentrations of DEHA. We determined the pseudo first-order decay constant for OH as a function of added DEHA by following the OH optical absorption spectrophotometrically, using a fast transient waveform digitizer with direct connection to our Sigma 5 computer. With aqueous studies it is possible to probe more powerfully into reaction mechanisms and intermediate detection and identification than is possible with gas-phase systems. Aqueous studies may also provide information on the deposition of DEHA in natural watersheds and conceivably in aqueous aerosols as well.

Our gas-phase system consisted of a Febetron electron source (a pulse of ~2-Mev electrons with a duration of 30 to 50 nsec) to excite a sample of humidified Ar gas containing DEHA (DEHA, 25 to 300 mtorr; H_2O, 15 torr; total pressure, 760 torr; temperature, 308 K). The Ar absorbs a small fraction of the electron beam energy and by highly efficient Ar-H_2O energy transfer processes and very short-lived ionic reactions causes the dissociation of H_2O vapor to OH and H. The electron pulse generates an initial yield of $10^{-6}M$ OH and H as the only long-lived (half-life >100 nsec) products of the radiation damage.

The OH is observed as its strong absorption line at 308.99 nm. The early transient chemistry is dominated by the decay processes given by Eqs. 1 through 5, where M designates an energy sink, either Ar or H_2O in this system:

$$OH + OH \xrightarrow{M} H_2O_2 \qquad (1)$$

$$OH + H \xrightarrow{M} H_2O \qquad (2)$$

$$H + H \xrightarrow{M} H_2 \qquad (3)$$

$$OH + DEHA \longrightarrow H_2O + R_1 \qquad (4)$$

$$H + DEHA \longrightarrow H_2O + R_2 \qquad (5)$$

In the absence of DEHA the OH decay is slow and second-order with respect to OH. With the addition of DEHA the OH decay is rapid and pseudo first-order, and varies linearly with the DEHA concentration as shown in Fig. 1. These results yield a biomolecular rate constant for the reaction of OH and DEHA at 308 K of 6.1×10^{10} M^{-1} sec^{-1} (1.0×10^{-10} cm^3 $molecule^{-1}$ sec^{-1}). Thus far, we have not been able to detect any absorption attributable to intermediates or products of the gas-phase reaction between OH and DEHA.

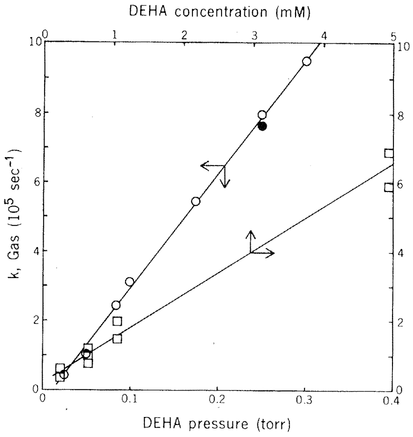

Fig. 1. Calculated pseudo first-order rate constants for the reaction OH + DEHA as a function of added DEHA. Data for the gas phase were measured in terms of the OH decay rate: (○) purified DEHA, (●) unpurified DEHA. Data for the aqueous phase were measured in terms of the formation rate of R_1: (□) purified DEHA. See text for experimental conditions.

For the aqueous studies we used the Argonne linac (4- to 40-nsec pulse of 12-Mev electrons) with samples of triply distilled water saturated with N_2O (to convert e^-_{aq} to OH by the rapid step shown as Eq. 6) and containing 0.2 m*M* to 5.0 m*M* DEHA at 300 K.

$$e^-_{aq} + N_2O \rightarrow N_2 + OH + OH^- \qquad (6)$$

The *p*H was adjusted to 9 to minimize the protonation of DEHA. Observation of OH at wavelengths less than 280 nm was hindered by interference from one or more transient absorptions; however, we were able to get a very approximate rate constant for the OH-DEHA reaction of 3×10^9 M^{-1} sec^{-1}. Using the streak camera system (*7*) for transient detection (wavelength span, 240 to 580 nm; observation time, up to 200 μsec after the pulse), we observed a broad absorption with a maximum at 400 nm that grows in as the OH decays, the formation being kinetically first order (see Fig. 1). It appears likely that this transient is the R_1 species or a product of its rapid isomerization. With this assumption we calculate that k (OH + DEHA, aqueous, 300 K) = 1.3×10^9 M^{-1} sec^{-1}. This value is in good agreement with results we obtained by the thiocyanate competition method (*8*) as well as with the approximate value from the OH decay. The thiocyanate results will be discussed elsewhere (*9*). The 400-nm species ultimately decays by a second-order process, independent of the DEHA concentration and the initial yield of OH, which is indicative of a radical-radical recombination or disproportionation reaction. Assuming that the maximum yield of this species is equal to the initial OH yield, we determine the molar extinction coefficient to be 390 M^{-1} cm^{-1} at 400 nm and calculate a rate constant for the decay of $2k = 8.2 \times 10^8$ M^{-1} sec^{-1}.

The gas-phase results demonstrate that DEHA and OH react in an extremely facile process, one which occurs on every third collison. In view of the significance of OH-hydrocarbon reactions in polluted air and the very high OH-DEHA reactivity, atmospheric release of DEHA would be expected to block the OH-hydrocarbon reactions if it were maintained in a relatively high steady-state concentration with respect to non-methane hydrocarbon (NMHC) concentrations. For a very smoggy day with 0.24 part per million (ppm) of NMHC and an "average" OH rate constant with NMHC of 5×10^9 M^{-1} sec^{-1}, this would correspond to about 0.2 ppm of DEHA for a 10 : 1 competition of DEHA to NMHC for the OH. The ultimate effect on the smog situation, that is, on the conversion of NO to NO_2 and on the production of O_3 and peroxyacetyl nitrate (PAN), will be a function of the effect DEHA has on the reactive radical (OH, HO_2, or other radicals) steady-state concentrations and the reactivity of the DEHA degradation products.

Morris and Niki (*10*) have demonstrated that the smog reactivity of many compounds is strongly correlated with the reactivity with OH. Thus, for DEHA to behave differently from a normal pollutant, it must be effective at terminating the smog-producing chain reactions and also must inhibit hydrocarbon degradation. Constant removal of the OH radical by continuous DEHA injection from early morning as well as downwind replenishing should prevent attainment of normal radical yields in the polluted air parcel. With this situation the primary pollutants and the DEHA decomposition products would be exposed to "low level" reactive radical conditions. Cessation of DEHA injection too early in the morning could result in a transition to "high level" radical conditions and consequent aggravation of the smog situation. Indeed, a recent study by Pitts and his co-workers (*11*) appears to demonstrate just this effect. Using a dual smog chamber with or without DEHA in ambient or surrogate polluted air, they found that low DEHA concentrations act as an additional pollutant. At 0.5 ppm of DEHA, there was an initial 1-hour inhibition of smog and then subsequently higher pollution levels than in the control case. At very high DEHA concentrations, inhibition was effective for the entire 6-hour experimental period. In all these experiments DEHA was added initially and allowed to decay away. The kinetic results reported here predict that DEHA maintained at 0.1 to 0.2 ppm for the entire experimental period could produce total inhibition of smog. It would be very interesting to test this hypothesis.

Our preliminary mechanistic information is consistent with OH abstraction of the H of the DEHA hydroxyl group in both the aqueous and gaseous phases, as opposed to the abstraction of the H of the ethyl groups or OH addition to DEHA. The results from studies in aqueous solution indicate a rapid reaction between OH and DEHA but one that is well below the diffusion-controlled rate. This result implies that hydration of the DEHA decreases the probability of a reactive encounter. This would be the expected result if the OH abstracts the H of the DEHA hydroxyl group and the oxygen atom of DEHA is the site of hydrogen bonding to the solvent. The solvent would then act to shield the H of the DEHA hydroxyl group from attack by OH.

We are presently investigating the gas-phase reactivity of HO_2 (*12*) and H with DEHA and determining the absorption spectra of the products of the primary processes. Our aqueous studies have been extended to include other means of measuring OH rates and of determining DEHA reactivity with e^-_{aq}, CO_3^-, and O_x^-. We are making further attempts to identify the intermediates and final products, using the techniques of chemically induced dynamic electron polarization (CIDEP), chemically induced dynamic nuclear polarization (CIDNP), electron spin resonance, and nuclear magnetic resonance coupled with pulse radiolysis (*9*).

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β-Endorphin and Adrenocorticotropin Are Secreted Concomitantly by the Pituitary Gland

Abstract. *The opiate-like peptide β-endorphin and adrenocorticotropin are concomitantly secreted in increased amounts by the adenohypophysis in response to acute stress or long-term adrenalectomy as well as in vitro in response to purified corticotropin releasing factor and other secretagogues. Conversely, administration of the synthetic glucocorticoid dexamethasone inhibits the secretion of both adrenocorticotropin and β-endorphin. Thus, both hormones possess common and identical regulatory mechanisms and there may be a functional role for circulating β-endorphin.*

The two biologically active polypeptides adrenocorticotropin (ACTH) and *β*-endorphin have been shown by Mains, Eipper, and Ling (*1*) originally to be part of a much larger precursor glycoprotein (31,000 daltons, referred to as 31K-precursor), as synthesized by the cloned pituitary cells of the (mouse) cell line AtT-20/D-16v. The common precursor concept is supported by earlier data on immunocytochemistry of normal pituitary tissue: ACTH [1–39] (residues 1 to 39); *β*-lipotropin (*β*-LPH [1–91]) the immediate endorphin-precursor, and the biologically active peptides *β*-endorphin (that is, *β*-LPH [61–91]) and *α*-endorphin (that is, *β*-LPH [61–76]) are all present in the same cells in the anterior and intermediate lobes of the pituitary gland (*2*). These observations raise the possibility that the biologically active forms of ACTH and *β*-endorphin might be normally secreted concomitantly. While work over the last 30 years has elucidated the physiological mechanisms involved in the secretion of ACTH, particularly as it relates to the response to stress, the recently discovered endorphins could not be studied in similar circumstances until specific methods to measure their concentration in blood or tissue extracts became available. We have recently devised, described, and validated such methodology (*3*). We now show that, in all conditions studied so far, ACTH and *β*-endorphin are secreted simultaneously by the pituitary gland.

Thirty-three male rats (Holtzman, 200 ± 15 g of body weight) were kept for 3 weeks, six animals per cage, with lights on at 0700 hours and off at 2000 hours. For studies on acute response to stress, each animal had the right tibia-fibula broken instantaneously, trunk blood being collected by decapitation in tubes containing EDTA (sodium salt) at intervals ranging from 60 seconds to 30 minutes. To study a possible adrenal steroid feedback mechanism on the secretion of endorphin, rats received dexamethasone acetate, a total of 12 mg over 12 days, in two daily subcutaneous injections; other animals were bilaterally adrenalectomized and maintained for 16 weeks on 1 percent NaCl as drinking fluid. Finally three rats from a larger pool of hypophysectomized animals were stressed and processed as above 10 months after total hypophysectomy.

As is shown in Fig. 1 and Table 1, plasma and pituitary concentrations of ACTH and *β*-endorphin vary concomitantly and in remarkable parallelism in all experimental situations described here, indicating that ACTH and endorphins are secreted simultaneously.

Hypophysectomy abolishes the response to stress, indicating that the peptides (*β*-endorphin and ACTH) measured in these studies are of hypophysial origin. Addition of purified corticotropin-releasing factor and of other secretagogues to monolayer cultures of adenohypophysial cells also stimulates concomitant secretion of immunoactive ACTH and *β*-endorphin (*4*). Thus it would appear that the regulatory mechanisms (hypothalamic releasing factor,