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quenching there is substantially less electronic energy to dissipate (63 versus 86 to 113 kcal/mole), albeit at greater mean relative collision velocities due to the higher temperature and smaller reduced mass. Exothermic Mg (3P_J) chemical quenching paths for CH₄ and H₂ (to produce MgH)⁹ are apparently inefficient, even at this high temperature, indicating the existence of substantial activation barriers. The results for C₆H₆ show that the availability of a triplet-state energy-transfer exit channel is not necessary for relatively efficient quenching by π -bonded molecules, since the first triplet state of benzene lies at an energy too high (~ 84 kcal/mole)¹⁰ to be sensitized by Mg (3P_J). Quenching of Cd (3P_J) and Hg (3P_J) by C₆H₆ and C₂H₄ almost certainly produces an excited molecular triplet state at effectively every collision.^{1,7,11}

The pulsed dye-laser method reported here can be extended to direct studies of the quenching and chemical reactivity of excited states of other metal atoms, and of short-lived molecular states selectively sensitized by excited metal atoms.

Water vapor dependence of the kinetics of the self-reaction of HO₂ in the gas phase*

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The hydroperoxo radical is an important intermediate in atmospheric and combustion chemistry. The gas phase self-reaction of HO₂



is thought to be important in both the normal¹ and polluted² troposphere, and its critical importance as a reference reaction for the many laboratory studies which measure rate constants relative to k_1 has been emphasized.³ Measurements of the rate of Reaction (1) at ≈ 298 K have been reported⁴ by Foner and Hudson⁵ (no H₂O present), $k_1 \sim 3 \times 10^{-12}$ cm³/molecule · sec, by Paukert and Johnston⁶ (no H₂O present), $k_1 = 3.6(5) \times 10^{-12}$ cm³/molecule · sec, and by Hochenadel *et al.*⁷ (21 torr H₂O present), $k_1 = 9.5(8) \times 10^{-12}$ cm³/molecule · sec. The latter two reports also included observation of the uv spectrum of HO₂, with good agreement on the spectral shape and maximum ($\lambda_{\text{max}} = 205\text{--}210$ nm), but a substantial difference in absorption cross section (base e): $\sigma_{\text{max}} = 4.5 \times 10^{-18}$ cm²/molecule⁶ and $6.8(6) \times 10^{-18}$ cm²/molecule.⁷ I report here pulse radiolysis experiments which show the previously unrecognized dependence of k_1 measurements on the amount of water vapor present.

The gas phase pulse radiolysis experiments with kinetic optical spectrophotometric detection were carried out using a model 705 Febetron and the apparatus developed by Gordon, Mulac, and Nangia,^{8,9} except that

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[†]Camille and Henry Dreyfus Foundation Teacher-Scholar.

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the analyzing light source was an unpulsed Hanovia 1 kW Hg-Xe compact arc lamp, and the photomultiplier signal was stored in a Biomation model 8100 transient recorder. The HO₂ transient absorption was observed at 230.5 nm, with a spectral resolution of 1.7 nm, and a path length of 40 cm. A Cl₂ filter in the light beam reduced the scattered light contribution to $\leq 0.8\%$ of the total signal.

Mixtures of 5 torr O₂ plus 0–15 torr H₂O in 2 atm H₂ were radiolyzed at 295(1) K with $a \leq 50$ ns pulse of electrons of ≈ 1.5 MeV incident energy. The calculated^{6,10,11} maximum temperature increase due to the pulse is ≤ 1.2 K. Using the known rate constants¹² for the reactions OH + H₂ \rightarrow H₂O + H and H + O₂ + H₂ \rightarrow HO₂ + H₂, the half-life in this system of OH is ≈ 2 μ s, and that of H is ≈ 1.6 μ s. Transient absorption was observed in the range 225–250 nm; the wavelength dependence of the maximum absorbance was consistent with the known HO₂ spectral shape.^{6,7} The formation of this HO₂ transient absorption was independent of [H₂O] and was essentially complete after 10 μ s. The magnitude of the maximum signal (transmittance ≈ 0.90) was likewise independent of [H₂O]. However, the HO₂ decay (first $t_{1/2} > 60$ μ s for all cases), which was always second-order during the 90%–95% observed, did depend on [H₂O], as shown in Fig. 1. The size and decay of the HO₂ transient absorption in 5 torr O₂ + 2 atm H₂ were unchanged by adding 10

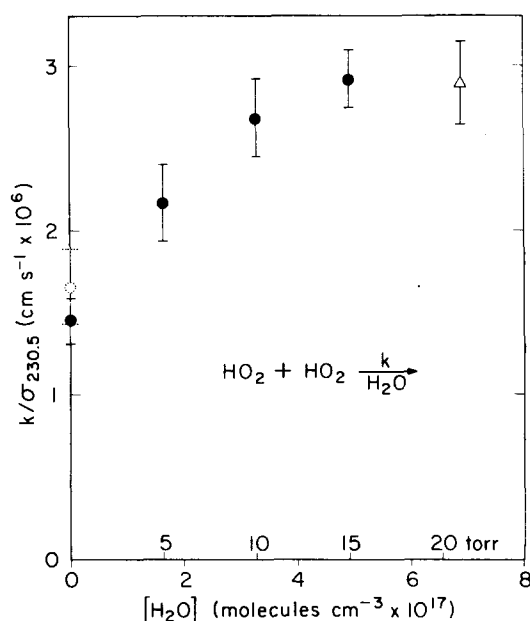


FIG. 1. Values of $k/\sigma_{230.5}$ for second-order reaction of HO_2 , as a function of H_2O concentration. •: this work; ○: derived¹³ value from Ref. 6; Δ: derived¹³ value from Ref. 7.

torr CH_4 ; however, the addition of 10 torr NH_3 increased the rate of the still second-order decay by about a factor 2.5, while leaving the size of the transient absorption unchanged. For all the above mixtures, the observed transient absorption was unchanged for at least three pulses of the same sample.

Figure 1 shows the measured $k/\sigma_{230.5}$ values from this work as a function of $[\text{H}_2\text{O}]$, together with the $k/\sigma_{230.5}$ value¹³ from each of the two earlier optical studies.^{6,7} Note that all data in Fig. 1 are independent of what the correct value of σ_{max} for HO_2 may be. Good agreement of this work with Paukert and Johnston⁶ at $[\text{H}_2\text{O}] = 0$ is obtained, while a smooth extrapolation could connect with the datum of Hochanadel *et al.*⁷ Clearly, only those rates measured in the absence of H_2O apply to the elementary Reaction (1). As mentioned earlier, the two determinations^{6,7} of σ_{max} for HO_2 differ substantially. The spectrum of Paukert and Johnston⁶ is accepted here because: (1) it leads to k_1 values in very good agreement with the value determined using mass spectrometry by Foner and Hudson⁵; (2) it overlies almost perfectly the aqueous solution spectrum of HO_2 ¹⁴ when both are plotted as a function of frequency and the latter is shifted by 4500 cm^{-1} to higher frequency; and (3) it agrees reasonably well with the HO_2 spectrum determined at 1100 K, when quantitative allowance is made for the differing vibrational state populations.¹⁵ We have then $\sigma_{230.5} = 2.17 \times 10^{-18}\text{ cm}^2/\text{molecule}$,⁶ which gives for this work $k_1 = 3.15 \times 10^{-12}\text{ cm}^3/\text{molecule} \cdot \text{sec}$, in very good agreement with the relevant earlier work.^{5,6}

The available data are insufficient to permit a full explanation of the effect of H_2O (and NH_3) on the observed

rate of second-order HO_2 decay—nevertheless, some conclusions are possible. The observation of this phenomenon only with polar gases (with hydrogen-bonding potential) indicates that a termolecular reaction with a simple energy-transfer mechanism¹⁶ is not operative. Also, the reaction $\text{HO}_2 + \text{HO}_2 \rightarrow \text{HO}_4\text{H}$ is ruled out by the estimated thermodynamic instability of HO_4H .^{17,18} It is very probable that association between HO_2 and H_2O is involved. The calculated high dipole moment of HO_2 [2.3(2)D¹⁹; 2.238D²⁰] lends support to this hypothesis. Because of (1) the constant transient spectral shape in the presence⁷ and absence⁶ of H_2O , (2) the constant size of the transient absorption in this work, independent of added H_2O (and NH_3), and (3) the absence of any *a priori* expectation of a substantial dependence of HO_2 yield on added H_2O (or NH_3) in this work, it is concluded that either $[\text{HO}_2] \gg [\text{complex}]$ in these experiments, or $\sigma(\text{HO}_2) = \sigma(\text{complex})$, or both. Therefore, the observed variation of $k/\sigma_{230.5}$ (Fig. 1) is due to variation of k .

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