action between the phosphate groups and the mercuric ions Hg^{++} and $HgCl^{+}$ about which we have no information.

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The Photochemical Formation of Ozone. Foreign Gas Effects on the Mercury Sensitized Reaction at 2537 Å. and the Unsensitized Reaction at 1849 Å.

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Following the formation of $Hg(^3P_1)$ atoms by adsorption of mercury resonance radiation, 2537 Å., three processes ultimately leading to ozone formation may be considered[1,2]

$$Hg^* + O_2 \longrightarrow Hg + 2O,\ \Delta H = 5.5 \text{ kcal.} \qquad (1)$$

$$Hg^* + O_2 \longrightarrow HgO(g) + O,\ \Delta H = -87 + \lambda \qquad (2)$$

$$Hg^* + O_2 \longrightarrow Hg + O_2^* \qquad (3)$$

where λ is the heat of sublimation of HgO(s). The calculations are based on $Hg(^3P_1)$ atom but the essential features would not be changed by considering instead $Hg(^3P_0)$. The activated oxygen species may be either normal oxygen molecules in high vibrational states or electronically excited oxygen.[3]

Calculations from collision theory based on the endothermicity of eq. 1 indicate that only one collision in about 10^4 would be effective. Since the quantum yield for the reaction is of the order of 0.03,[4] and since long chains are not possible, it appears unlikely that this reaction is an important one.

The value of λ for eq. 2 is not known but Noyes[5] estimates that it is not over 23 kcal. Thus (2) is exothermic, and therefore (2) and (3) are both possible paths. Dickinson and Sherrill[6] have shown that at least 7 molecules of ozone are formed for each mercury atom passing through the reaction zone. Volman[4] has evidence that this value may actually be considerably higher. Since the formation of ozone from oxygen is 34 kcal. endothermic, a single activated mercury molecule can at best account for 3 ozone molecules. This could possibly be as high as 4 if the heat evolved in the formation of HgO were available. Even these yields are unlikely since mechanisms giving these values do not appear probable. A postulated solution to this dilemma is the reaction[3]

$$HgO(g) + O_2 \longrightarrow Hg + O_3$$

However this reaction is endothermic to the extent of 68-λ kcal.

The troublesome features of (1) and (2) are largely obviated in (3). Activated oxygen produced may react by

$$O_2^* + O_2 \longrightarrow O_3 + O \qquad (4)$$

followed by

$$O + O_2 + M \longrightarrow O_3 + M \qquad (5)$$

Equation 5 is common to mechanisms involved in (1), (2) and (3) since O atoms are postulated for all three.

It was felt that a study of the effects of foreign gases in the reaction system would give information relative to the mechanism of ozone production since foreign gases would play a role in the following processes

$$Hg^* + M \longrightarrow Hg + M^* \qquad (6)$$

$$O_2^* + M \longrightarrow O_2 + M^* \qquad (7)$$

as well as in eq. 5 above. In the course of the experiments, it became evident that information on the effects of foreign gases on the unsensitized reaction would also be desirable.

Experimental

The experimental flow method used was similar to that described earlier.[7] High purity commercial gases from cylinders were measured by flow meters and dried over magnesium perchlorate. The light source was a mercury–rare gas low pressure discharge tube in the shape of a helix, 70 mm. across and 250 mm. long. The light emitted from such a lamp is primarily a mixture of the 1849 and 2537 Å. mercury resonance lines. Since the 1849 Å. line will not be transmitted through a few mm. of liquid water,[8] it is possible to prevent the short wave length radiation from reaching the reaction zone. For the unsensitized reaction, the lamp and reaction tube, 30 mm. diam., were both surrounded by air. Under these conditions ozone was formed in the absence of mercury vapor. For the sensitized reaction, the reaction vessel, 20 mm. diam., and surrounding lamp were contained in a water-bath thermostated at 45°, the temperature for optimum light intensity.[8] Under these conditions ozone was not formed in the absence of mercury vapor but was formed in the presence of mercury vapor. The pressure of mercury vapor entering the reaction zone was adjusted to a value corresponding to saturation at 20° in the manner described previously.[7] Since oxygen gas at atmospheric pressure can absorb only negligible amounts of light of wave length 2537 Å., the formation of ozone in the unsensitized reaction may be attributed primarily to the absorption of the 1849 Å. resonance line by oxygen molecule. Ozone in the effluent gases was determined iodimetrically after absorbing in a neutral potassium iodide solution.

Results and Discussion

Number of Cycles Involving Mercury Vapor.—In the sensitized reaction a red-orange deposit of mercuric oxide was observed in agreement with the results of Dickinson and Sherrill.[6] This deposit was heaviest at the entrance to the reaction zone and tapered off so that no deposit was observable after about 8 cm. The effluent gas was found to be free of mercury vapor. From the yield of ozone and the vapor pressure of mercury entering the reaction zone, a value for the number of ozone molecules formed for each mercury atom entering the reaction zone may be determined. For example, at a flow rate of 1.0 liters oxygen per minute, the yield of ozone was 4.2×10^{-6} mole per minute. The gas stream contained mercury equivalent to saturation vapor pressure at 20.0°. Thus for each mercury atom about 60 molecules of ozone were

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[1] Other processes involving postulated but not established molecular species have sometimes been considered, *i.e.*, HgO_2. *Cf.* W. A. Noyes, Jr., THIS JOURNAL, **49**, 3100 (1927).

[2] Thermochemical values from F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of Chemical Substances," Reinhold Publ. Corp., New York, N. Y., 1936.

[3] W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941, p. 225.

[4] D. H. Volman, *J. Chem. Phys.*, **21**, 2086 (1953).

[5] W. A. Noyes, Jr., THIS JOURNAL, **53**, 514 (1931).

[6] R. G. Dickinson and M. S. Sherrill, *Proc. Natl. Acad. Sci.*, **12**, 175 (1926).

[7] D. H. Volman, *J. Chem. Phys.*, **14**, 707 (1946).

[8] L. J. Heidt and H. B. Bayles, THIS JOURNAL, **73**, 5728 (1951).

formed. From a thermochemical point of view each quantum can yield 3 ozone molecules and therefore each mercury atom must be optically activated a minimum of 20 times to account for these results. The actual number of fruitful cycles each mercury atom undergoes is probably considerably higher for a number of reasons: the probable mechanisms yield only 2 molecules of ozone per quantum; the actual quantum yield is low; considerable mercury is removed in the first few cm. of the reaction zone as mercuric oxide on the walls; and ozone is photochemically decomposed. For reasons already discussed, these results emphasize the improbability of a mechanism based on eq. 2.

Effects of Foreign Gases on the Sensitized Reaction.—The effects of foreign gases on the sensitized reaction are shown in Fig. 1. Although the ozone yield is increased with increasing flow rate, as is clearly shown by the experiments with oxygen alone or in helium mixtures, the comparative effects of the added gases are readily apparent. The zero point for all experiments is the ozone yield with an oxygen flow rate of 0.50 liter per minute without other gas. It is believed that these data are in accord with a mechanism represented by equations 3–7. Foreign gases may deactivate optically excited mercury atoms, deactivate excited oxygen molecules, or participate as a third body in the formation of ozone from oxygen atom and oxygen molecule. Mercuric oxide formation is explained by secondary reactions from ozone and mercury.

The quenching efficiencies for $Hg(^3P_1)$ of the various gases used in this study are given in Table I. The relative quenching efficiencies were calculated from the quenching cross sections[9] by dividing by the square root of the reduced mass. The quenching efficiencies are given relative to oxygen taken as unity.

TABLE I

RELATIVE QUENCHING EFFICIENCY FOR $Hg(^3P_1)$

Gas	Effective collisional cross-section, cm.^{2} $\times 10^{16}$	Relative quenching efficiency
He	0.0	0
A	0.0	0
N_2	0.274	0.015
CO_2	3.54	0.16
O_2	19.9	1.00

From these relative efficiencies of activated mercury quenching it would be expected that, except for carbon dioxide at the highest added gas pressures used, the foreign gases would deactivate only a small fraction of activated molecules. Since argon and helium are non-quenchers,[10] the difference in the effects of these two gases are certainly not explicable by (6) but instead by (5) and (7). Although the argument is not so strong for N_2 and CO_2, the effects of mercury quenching by these gases appear small over most of the flow-rate region used.

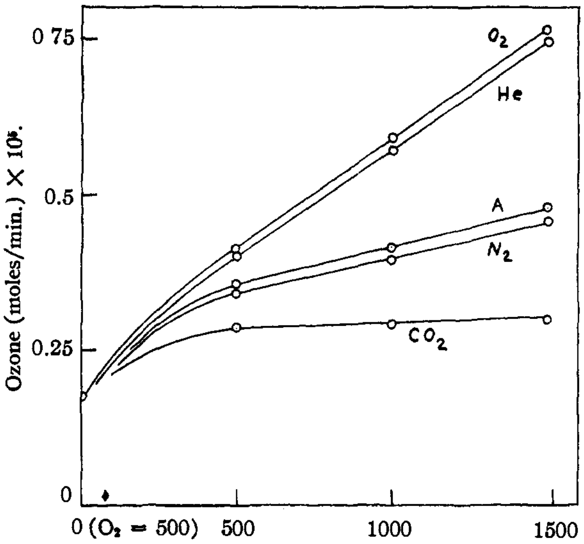

Fig. 1.—Sensitized reaction; effects of added gases on ozone yield.

Effects of Foreign Gases on the Unsensitized Reaction.—The effects of foreign gases on the unsensitized formation of ozone in the short ultraviolet region has received only fragmentary attention. Thus Groth[11] has found that the rate of ozone formation is about the same in mixtures of oxygen and argon as in mixtures of oxygen and nitrogen. The effect of foreign gases on the photodecomposition of ozone in the ultraviolet region has received considerably more attention.[12–14] Although the comparative effects of gases on the photodecomposition could be used to make predictions on the effects of foreign gases on the synthesis of ozone, since the results are largely explained by the effect of the foreign gas on reaction (5) for both processes, it was felt that a direct determination of the foreign gas effects for the synthesis would be valuable. The results obtained in this study are shown in Fig. 2.

These results are consistent with the ones obtained for the photo-decomposition. That is, gases which tend to prevent the photodecomposition by acting as efficient third bodies in reaction 5 also tend to promote the photosynthetic reaction for the same reason since absorption at 1849° Å. yields oxygen atoms either directly or by predissociation.

Comparison of Sensitized and Unsensitized Results.—Comparing the unsensitized results with the sensitized results, the effects of the foreign gas are in exactly opposite order. In terms of the probable mechanism, this means that the deactivating effect of the foreign gases on reaction (7) of the photosensitized mechanism is partly counteracted

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[9] A. C. G. Mitchell and M. W. Zemansky, "Resonance Radiation and Excited Atoms," Cambridge University Press, London, 1934, p. 204.

[10] The collisional deactivation of excited electronic states of atoms is very improbable unless energy resonance can occur. This is not possible in collisions between mercury and rare gases since the energy difference between the ground and first excited electronic level of the rare gases is much greater than for the corresponding transition in mercury. *Cf.* P. Pringsheim, "Fluorescence and Phosphorescence," Interscience Publishers, Inc., New York, N. Y., 1949, pp. 91, 99.

[11] W. Groth, *Z. physik. Chem.*, **B37**, 307 (1937).

[12] H. J. Schumacher, THIS JOURNAL, **52**, 2377 (1930).

[13] U. Beretta and H. J. Schumacher, *Z. physik. Chem.*, **B17**, 417 (1932).

[14] D. H. Volman, THIS JOURNAL, **73**, 1018 (1951).

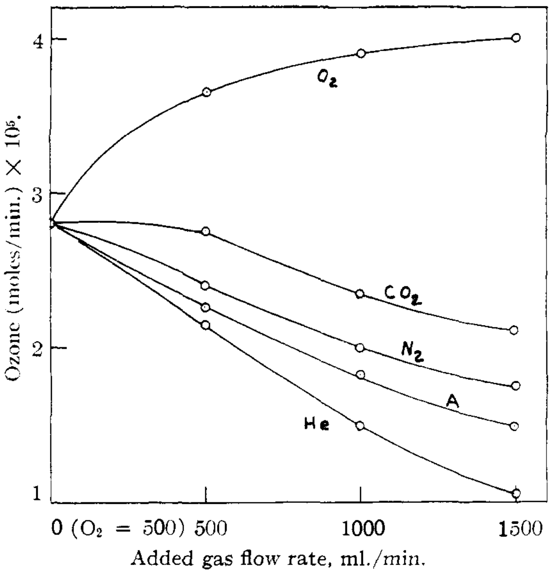

Fig. 2.—Unsensitized reaction; effects of added gases on ozone yield.

by the effect of the foreign gases on reaction (5) common to both the sensitized and unsensitized mechanism. In this competition, the effects of the foreign gases on reaction (7) more than overcome the effects on reaction (5) for the sensitized reaction. This result would be expected as a consequence of the greater probability of two body over three body collisions apart from any other consideration.

If one assumes that the entire effect of the foreign gas for the sensitized reaction is on reaction (7), the relative values of rate constants for the various gases in this reaction is approximately: CO_2, 1; A, 0.6; N_2, 0.6; He, 0.05. These values are in good agreement with those which may be calculated from the data of Holmes and Daniels,[15] for foreign gas effects on the photodecomposition of NO_2 where the postulated foreign gas effect is likewise the deactivation of an excited molecule, in this case NO_2. The order observed is also in agreement with that expected from the discussion of Russell and Simons[16] indicated that the effects are primarily determined by the magnitudes of the intermolecular force fields and therefore parallel the magnitudes of the van der Waals forces, the boiling points and the critical temperatures.

(15) H. H. Holmes and F. Daniels, THIS JOURNAL, **56**, 630 (1934).

(16) K. E. Russell and J. Simons, *Proc. Roy. Soc. (London)*, **A217**, 271 (1953).

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Light Scattering of Isoionic Bovine Albumin[1]

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The interpretation of light scattering measurements from two-component systems, *e.g.*, a salt-free protein and water, is simpler than if supporting electrolytes are added. A comparative study of bovine plasma albumin in water and in 0.15 *M* sodium chloride is presented. For this protein in the absence of salt, the extrapolation of intensities for molecular weight (*M*) determination appears to be straightforward and yields values of *M* in close agreement with other methods. The data suggest that values of *M* obtained in sodium chloride solutions may occasionally be elevated by an impurity which aggregates in the absence of salts and can be removed by high speed centrifugation or suitable filtration in water alone. The techniques described here can quite probably be used advantageously for studying salt-free solutions of other proteins which can be deionized by ion exchange or electrodialysis.

Light scattering measurements for the determination of the molecular weights of proteins are usually carried out in the presence of electrolytes added to suppress the effects of electrostatic charge. The addition of supporting electrolyte to a protein solution results in at least a three-component system, or if a buffer is used, in a four-component system. Equations to describe the small particle scattering from multi-component systems have been derived by several groups of workers[2-4] and have been applied to proteins by Edsall, *et al.*,[5] in approximately the following form

$$2R_{90,\mathrm{u}} = \frac{K'' \sum_{i} \sum_{j} \psi_{\mathrm{i}} \psi_{\mathrm{j}} A_{\mathrm{ij}}}{|a_{\mathrm{ij}}|} \tag{1}$$

In eq. 1, $R_{90,\mathrm{u}}$ is the excess scattered intensity observed at 90° with unpolarized incident light and $K'' = 4000\ \pi^2 n^2/\lambda_0^4 N_0$ where n is the refractive index, λ_0 the wave length *in vacuo* and N_0, Avogadro's number; ψ stands for molar refractive increment. The terms a_{ij} in the determinant $|a_{\mathrm{ij}}|$ are the derivatives $\partial \ln a_{\mathrm{i}}/\partial m_{\mathrm{j}}$ where a is the activity and m the molar concentration. The term A_{ij} in the double summation is the cofactor of the term a_{ij}, *i.e.*, the determinant obtained from $|a_{\mathrm{ij}}|$ by striking out the row and column in which a_{ij} occurs and multiplying the resulting determinant by $+1$ if $i + j$ is even and by -1 if $i + j$ is odd.

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(1) The results presented here have been previously reported in part at the 38th annual meeting of the American Society of Biological Chemists, April, 1954; W. B. Dandliker, *Federation Proc.*, **13**, 196 (1954). After these results were substantially in their present form, a report of very similar experiments appeared from Professor Kirkwood's laboratory.[12] In addition, the author learned that Professor J. T. Edsall and Dr. R. H. Maybury had carried out some unpublished work along these lines in the summer of 1953. This work has been supported by funds from Initiative 171, State of Washington. Invaluable technical assistance was given by Mr. Nozar Pirzadeh.

(2) H. C. Brinkman and J. J. Hermans, *J. Chem. Phys.*, **17**, 574 (1949).

(3) J. G. Kirkwood and R. J. Goldberg, *ibid.*, **18**, 54 (1950).

(4) W. H. Stockmayer, *ibid.*, **18**, 58 (1950).

(5) J. T. Edsall, H. Edelhoch, R. Lontie and P. R. Morrison, THIS JOURNAL, **72**, 4641 (1950).