ane in the temperature range immediately above 89°K. and those of solid methane for temperatures below 89°K. However, in the range of temperatures covered by the work, there does not appear to be any significant trend in the value of the heat capacity as the coverage is increased from 0.2 to 1.0 monolayer. The fact that the heat capacity of the adsorbed methane is greater than that of solid methane may be due in part to the effect of a phase transition from localized to mobile adsorption. Hill[4] has shown for a simple theoretical model which neglects the interaction of the molecules and the effect of the heterogeneity of the surface that such a transition would occur at temperatures below 90°K. In this case, the contribution to the heat capacity by the transition is determined by the shape and magnitude of the potential barrier restricting the movement of the molecules over the surface of the solid.

The scope of the present measurements is too limited to propose a complete model for the adsorption. Hill[12] has considered the case of a molecule localized on a heterogeneous surface. The energy of such a molecule is dependent on (1) the partition function for the three vibrational degrees of freedom of the center of mass plus the usual internal degrees of freedom, (2) the distribution of energy at the solid sites, (3) the lateral interaction of the adsorbed molecules. The heat capacity of the adsorbed phase is determined by the temperature dependence of all these factors. The distribution of energy at the solid sites, evaluated from measurements of adsorption isotherms and heats of adsorption, as well as theoretical considerations such as the variation of the internal partition function with the energy of the sites are necessary for the description of the complete model.

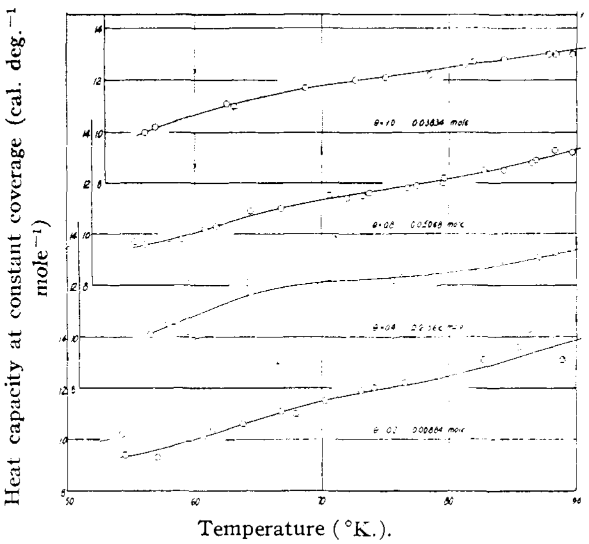

Fig. 1.—Molar heat capacity of methane adsorbed on titanium dioxide (rutile) at various coverages.

Acknowledgment.—We are indebted to the Office of Naval Research for the support provided under Contract No. N7-onr-47003 and to the Atomic Energy Commission for the support under Contract No. AT(30-1)-824. Dr. S. S. Cole of the National Lead Company was kind enough to furnish us with the samples of titanium dioxide used in the work.

CLEVELAND, OHIO

---

[12] T. L. Hill, *J. Chem. Phys.*, **17**, 762 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CANISIUS COLLEGE]

The Radiation Decolorization of Dilute Dye Solutions; Chlor Phenol Red[1,2]

BY EDWARD N. WEBER AND ROBERT H. SCHULER

RECEIVED FEBRUARY 28, 1952

The kinetics of the decolorization processes induced in dilute aqueous solutions of chlor phenol red by X-radiation of 120 kev. energy has been investigated. The reactions are secondary to the absorption of the radiation by the water and subsequent formation of active intermediates. The molecule, which results from the initial decolorization has a susceptibility for further reaction approximately equal to that of the original species. The relatively low yield for decolorization suggests that reaction of the dye molecule does not necessarily result in decolorization. The properties of this system are such as to provide a good model for the radiation chemistry of enzyme and related systems. Competition of thiourea for the radiation intermediate has been observed.

Application of X-ray decolorization of solutions of methylene blue in radiation dosimetry has been previously discussed[3-5] and the X-ray induced reactions of numerous other colored organic materials have also been qualitatively described.[6] We have had occasion, in an examination of chemical actinometers for radiation decomposition studies in progress, to study the kinetics of the decolorization reactions of dilute aqueous solutions of chlor phenol red. The results of this investigation, although indicating that these decolorization reactions are not suitable for accurate actinometric purposes, do have a bearing on the radiation chemistry of aqueous systems. Because of the low concentrations involved, aspects may be regarded as quite analogous to certain radio-biological processes.

Experimental

The unfiltered radiation from an industrial 60–140 kev. X-ray unit was used as the source of activation. The instrument was operated at constant intensity characterized by a current of 5 ma. at 120 kev. energy, the effective

---

[1] Presented at the 119th National Meeting of the American Chemical Society, Cleveland, Ohio, April 8-12, 1951.

[2] This work was supported, in part, under contract AT(30-1)-1084 with the U. S. Atomic Energy Commission.

[3] W. Stenstrom and H. R. Street, *Proc. Soc. Exptl. Biol. Med.*, **32**, 1498 (1935).

[4] W. Stenstrom and A. Lohman, *Radiology*, **16**, 322 (1931); **22**, 304 (1934).

[5] S. A. Goldblith, B. E. Proctor and O. A. Hammerle, *Ind. Eng. Chem.*, **44**, 310 (1952).

[6] G. L. Clark and K. R. Fitch, *Radiology*, **17**, 285 (1931).

wave length of the radiation being approximately 0.2 Å. The samples (10 ml.) were irradiated in 50-ml. florence flasks which were placed in a reproducible position in front of the X-ray window. The radiation entered vertically through the bottom of the cell. Since the absorption coefficient of water is not very great at these wave lengths, the radiation is absorbed quite homogeneously throughout the sample. All reactions were carried out at room temperature or slightly above.

The decolorization reactions produced by the X-radiation were followed by determining the optical densities of the solutions in 1-cm. cells with a Beckman DU spectrophotometer. The measurements were made at 570 mμ after the dye coloration had been developed by the addition of one drop of concentrated sodium hydroxide.[7] Above a *p*H of 10 the molar extinction coefficient, at 570 mμ, of the blue form of chlor phenol red is independent of the *p*H. This coefficient was determined to be 54,000 in a solution containing a weighed amount of the crystalline materials. It was found if the acid (yellow) form of the dye was used for analysis, that the absorption of product interfered with the determination at the maximum absorption at 435 mμ.

Crystalline chlor phenol red ($C_{19}H_{12}Cl_2O_5S$; dichlorophenolsulfonphthalein) obtained from the Fisher Scientific Co. was dissolved in freshly distilled water to give a relatively concentrated master solution, which was diluted as needed to the desired concentration. These solutions were quite stable toward the atmosphere over long periods of time. The unbuffered solutions were used at a *p*H of 6.0 to 6.5 in order that other materials need not be added to the system during the irradiation. Except where noted, the samples were saturated with air in equilibrium with the atmosphere. This dissolved air is sufficient to provide a very large excess of the required oxygen for the reactions involved.

Results

Solutions which contain the same initial concentration of dye show a decolorization which is not directly proportional to the radiation dosage, as might be expected, but rather one which falls off exponentially as the irradiation progresses. The decolorization resembles a first order reaction with each subsequent absorption of an equivalent amount of energy resulting in a successively equal fractional decolorization of the sample. When, however, one irradiates solutions containing different initial concentrations, the fractional decolorization for a given irradiation is found to be dependent upon the original concentration of dye present (Fig. 1). The initial rate (8.8×10^{-9} mole of dye reacting per minute) is approximately the same for these different samples, dropping off a little in the more dilute solutions. The rate is, therefore, of zero order but is modified by the extent of the decomposition as the reaction proceeds.

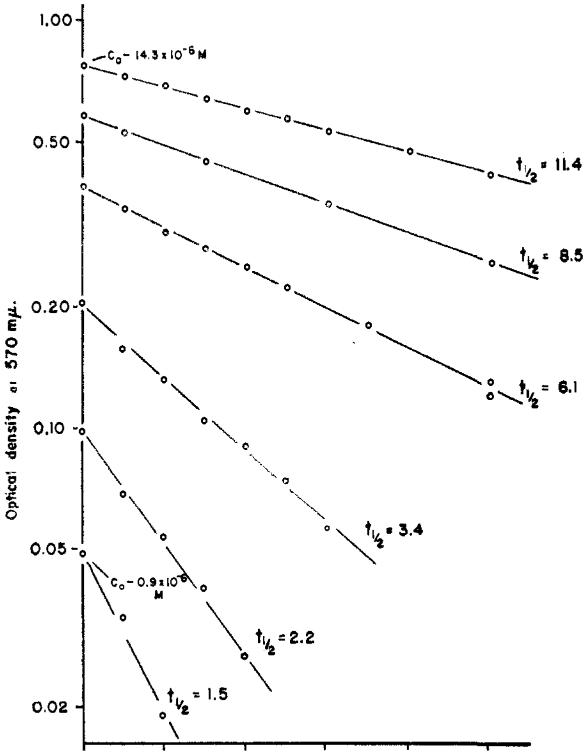

Fig. 1.—Decolorization of chlor phenol red solutions.

In Fig. 2 the period, at constant intensity, required for 50% decolorization is plotted as a function of the dye originally present. A linear relationship is shown which extrapolates to a positive intercept at zero dye concentration.

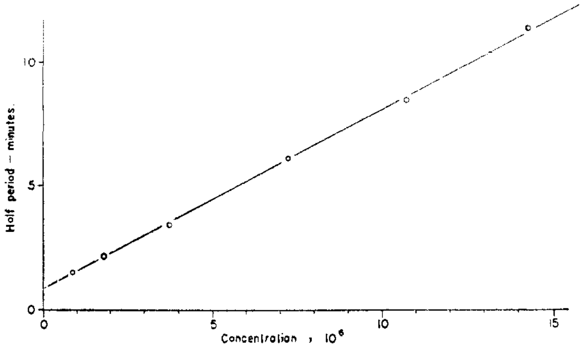

Fig. 2.—Irradiation period required for 50% decolorization of the dye.

If the fraction of the initial dye coloration is plotted as a function of the dosage, then different curves are obtained for the various solutions. If, however, the dosage is normalized by dividing by the initial concentration, then the values for the more concentrated solutions fall on a single curve (Fig. 3). At the lower concentrations, the values are high because of side reactions which are relatively more important at these concentrations. The side reactions retard the decolorization and lead to the positive intercept mentioned above. Equal fractional decolorizations of the samples result, therefore, from dosages which are proportional to the amount of the dye present in the sample. This general behavior is identical to that for the inactivation of carboxypeptidase reported by Dale.[8]

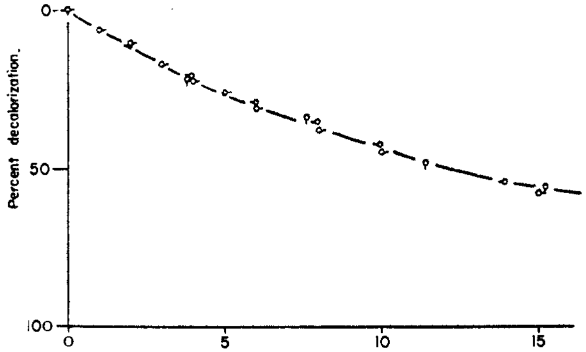

Fig. 3.—Decolorization as a function of dosage normalized by a factor of $C_0/(14.3 \times 10^{-6})$; o-, $C_0 = 14.3 \times 10^{-6}$; -o, $C_0 = 10.7 \times 10^{-6}$; ♀, $C_0 = 7.1 \times 10^{-6}$ *M*.

Various attempts were made to ascertain the effect of dissolved air on the reaction. Pumping of the gases from solution did not have any pronounced effect on the rate of decolorization, the maximum observed decrease in this

---

(7) For purposes of these experiments, decolorization is defined in terms of loss of optical density at 570 mμ.

(8) W. M. Dale, W. J. Meredith and M. C. K. Tweedie, *Nature*, **151**, 280 (1943); W. M. Dale, L. H. Gray and W. J. Meredith, *Phil. Trans. Roy. Soc. (London)*, **A242**, 33 (1949).

rate being about 10% for short irradiation periods. Deaeration of the sample by displacement with hydrogen decreased the rate by about 25%. In a series of experiments, during which hydrogen was bubbled through the sample and subsequently pumped from the system, the rate of decolorization was reduced to 40% of normal for short exposures and to about 20% after continued irradiation of one half to one hour. In other experiments, during which the sample was sealed from a high vacuum line after repeatedly boiling, freezing, and pumping the sample, the reaction rate was about 50% of normal. It was not possible, however, to reduce the radiation effect entirely to nil. It is concluded, therefore that, while the presence of dissolved oxygen seems to be required for part of the reaction, either the remainder of the reaction does not require oxygen or other decolorization processes are operative in the absence of the oxygen. Since very little ($\sim 10^{-7}$ mole) dye is actually involved here, a trace of oxygen or other reactive substance would be sufficient to have a pronounced effect.

A check of the effect of hydrogen peroxide shows that the dye is bleached only slowly when peroxide is present in relatively high concentrations, *e.g.*, in 3% peroxide solution the sample was 50% decolorized in 20 minutes. Since the amount of peroxide formed in these irradiations is very small, it seems unlikely that there is any indirect effect *via* the production of hydrogen peroxide but rather that the decolorization takes place with a more active agent prior to the formation of the peroxide.

Comparison with the oxidation of ferrous sulfate in 0.8 *N* sulfuric acid gives 6.54×10^{17} e.v./min. as the rate of absorption of energy by the chlor phenol red system. A yield of 0.81 (*G:* equivalents of reaction per 100 e.v. of absorbed energy) is thus observed for the initial decolorization rate. This is not dependent, except for the lowest concentrations, on the concentration of the dye. The *G* for the oxidation of ferrous sulfate has been assumed to be 15.5,[9] and the relative absorption of the ferrous sulfate taken as 1.1 times that of pure water for the wave lengths employed here.

In Fig. 4 the effect of the addition of sodium hydroxide and hydrochloric acid to the solution before irradiation is illustrated. The solutions, 15×10^{-6} *M* in dye, were irradiated for ten minutes and analyzed in the basic form. A maximum decolorization is observed at a *p*H of 3–4. The drop at low *p*H may, of course, be due to the presence of the chloride ion.

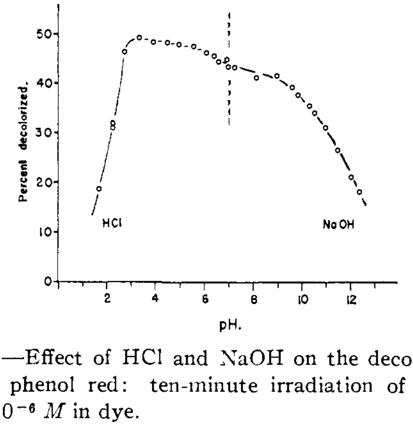

Fig. 4.—Effect of HCl and NaOH on the decolorization of chlor phenol red: ten-minute irradiation of solutions 14.3×10^{-6} *M* in dye.

The effect of foreign organic substances, such as thiourea, is seen in Fig. 5. When the latter is present at a concentration equal to that of the dye, approximately 25% "protection" (inhibition · of dye decolorization) is observed. The presence of 10^{-3} *M* thiourea gives better than 95% protection against decolorization of solutions 5×10^{-6} *M* in dye. Further investigations are in progress which utilize this protective effect as a method of studying the relative reactivities of other substances toward the radiation intermediates.

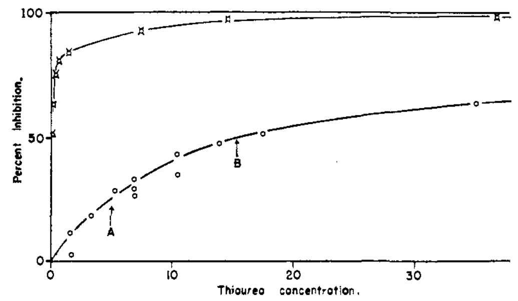

Fig. 5.—Effect of thiourea on the decolorization of chlor phenol red. Five minute irradiation of solutions 5.2×10^{-6} *M* in dye (A): lower curve, concentration $\times 10^6$; upper curve, concentration $\times 10^4$. B represents 50% inhibition at 16×10^{-6} *M* thiourea.

Discussion

The net primary result of the activation of dilute aqueous systems by X-radiation, *via* the production of secondary electrons in the water by the absorbed radiation, is the dissociation of the water into hydrogen atoms and hydroxyl radicals.[10]

$$H_2O \overset{G_pI_a}{\rightsquigarrow} H\cdot + OH\cdot \qquad (I)$$

In the above equation G_p represents the primary reaction yield in terms of molecules reacting per 100 e.v. absorbed by the sample and I_a the absorbed intensity in units of 100 e.v. per unit volume of sample.

Secondary effects, such as the decolorization reactions observed here, are produced by subsequent reaction of these radicals with the other components present. This type of decolorization is, therefore, completely different from photochemical bleaching where the primary activation occurs in the dye itself. When oxygen is present, the hydrogen atoms produced in reaction I will react to form $HO_2\cdot$ radicals and will be removed from further reaction.

$$H\cdot + O_2 \longrightarrow HO_2\cdot \qquad (II)$$

Thus, in the presence of oxygen, the radicals $HO_2\cdot$ and $OH\cdot$ are possible radiation intermediates which can cause decolorization of the dye.

The reaction of the active decolorizing agent may be represented as

$$R\cdot + \text{colored (D)} \xrightarrow{fk_3} \text{uncolored (D')} \qquad (IIIa)$$

$$R\cdot + \text{colored (D)} \xrightarrow{(1-f)k_3} \text{colored (D)} \qquad (IIIb)$$

where *f* corresponds to the fraction of the reaction which results in decolorization. As soon as part of the dye has been converted to the uncolored form, there will be further reaction of the type

$$R\cdot + D' \xrightarrow{k_4} D'' \qquad (IV)$$

Other reactions, involving the reaction of the radicals with each other and with other substances contained in the system either as impurities or additives, must also be considered. The importance of these various reactions will depend on the concentration levels of the dye and any other substance present.

---

(9) C. J. Hochanadel, Abstracts of papers, 119th Meeting of the American Chemical Society, Cleveland, Ohio, April 11, 1951; private communication.

(10) A. O. Allen, "The Science and Engineering of Nuclear Power," Chapter 13, Addison-Wesley Press, Inc., Cambridge, Mass., 1949.

$$R\cdot + M \xrightarrow{k_5} \qquad (V)$$

The rate of decolorization (reaction IIIa) will be given by

$$-\,d(D)/dt = fk_3(D)(R\cdot) \qquad (1)$$

If we substitute the steady state concentration of R·, obtained by assuming that steps III and IV are the only reactions removing this component, equation (1) becomes

$$-\frac{d(D)}{dt} = fk_3(D)\,\frac{G_pI_a}{k_3(D) + k_4(D')} \qquad (2)$$

which can be further reduced to the form

$$-\frac{d(D)}{dt} = fG_pI_a\,\frac{1}{1 + k_4(D')/k_3(D)} \qquad (3)$$

It is seen that the type of curve obtained for the decolorization as a function of the total sample dosage, will be determined by the importance of the term $k_4(D')/k_3(D)$ in the denominator of (3), *i.e.*, the extent of reaction and the relative susceptibility toward further reaction of the product of the original decolorization. Two of the simplest cases are illustrated below.

Case I.—If the product of the reaction is not reactive toward the radiation intermediate ($k_4 \sim 0$) or if it is at very low concentration, then the rate of decolorization will be dependent only on the reaction yield and the incident intensity and the reaction will be of zero order.

$$-\,d(D)/dt = fG_pI_a \qquad (4)$$

Case II.—If the product of the reaction has a reactivity equal to that of the original substance then

$$k_3(D) + k_4(D') \sim k_3(D_0) \qquad (5)$$

where (D_0) is the original dye concentration. Substituting this into equation (2) we obtain

$$-\,d(D)/dt = fG_pI_a[(D)/(D_0)] \qquad (6)$$

which upon integration gives

$$(D) = (D_0)e^{-fG_pI_a(t/(D_0))} \qquad (7)$$

$$\ln\frac{(D_0)}{(D)} = \frac{fG_pI_a}{(D_0)}\,t \qquad (8)$$

In this case, the response is seen to be exponential in form, characterized by a half period which is directly proportional to the original concentration.

$$t_{1/2} = \frac{0.693}{fG_pI_a}\,(D_0) \qquad (9)$$

In the general case, where the reaction of substances added to the solution before irradiation removes the active intermediates, by reactions other than III and IV, these reactions will be accounted for in terms similar to $k_4(D')$ in equation (2). The nature of the effect will depend on the variation of this term during the course of the reaction. The decolorization rate must, of course, be lessened by the removal of the active species by extraneous reactions.

The Decolorization of Chlor Phenol Red.—It is seen that the decolorization of chlor phenol red observed here, closely follows the logarithmic relationship of equation (8). The normalized plot of Fig. 3 illustrates equation (7), with fG_pI_a the same for all solutions. The half-period is found to be directly proportional to the initial concentration with, however, a constant term being added to equation (9) to account for reactions of type V. It is concluded that this reaction represents case II above, being such that the product of the reaction, although decolorized, is susceptible to further reaction with the radiation intermediate. The susceptibility of this product appears to be very nearly equal to that of the original dye. Exact equality is not had as is shown by the results of longer irradiations where a slight tendency for the curves to have a somewhat steeper slope is observed.

The yield of the initial decolorization reaction ($G_0 = 0.81$) deserves further mention as it is lower than might be anticipated from the primary yield estimated for aqueous decomposition, *i.e.*, greater than 3.3.[9] It seems, therefore, that only a fraction ($f \sim 0.25$) of the radiation intermediate reacts in such a manner as to decolorize the dye. This is in agreement with the non-specificity required by the approximate equality of the reactions of the original dye and the product substance. As far as decolorization is concerned, the dye is "self-protecting" for the reactions involved.

The effect of additives is, in general, illustrated by the behavior of the reaction in the presence of thiourea. The competition or protective effect of the thiourea is such as to indicate that the thiourea molecule is one-third as reactive as the dye. Dale, *et al.*,[11] report that thiourea is approximately 100 times as reactive as carboxypeptidase on an equal weight basis.

The general picture of the behavior of chlor phenol red solutions upon exposure to X-radiation is much the same as that given by Fricke and Peterson[12] for the oxidation of oxyhemoglobin and by the work of Dale already mentioned. The considerations employed here are almost identical to those of Weiss[13] on enzyme reactions. The decolorization reactions of the dyes suggest themselves as being applicable to formulation as models for the radiation reactions of enzyme and similar systems. The relative ease of the colorimetric determinations makes these reactions useful as such models in the study of the radiation chemistry of dilute aqueous solutions of organic substances.

Acknowledgment.—We wish to thank Professor Austin C. McTigue of the Physics Department for his coöperation in the loan of the X-ray equipment utilized here. We also wish to acknowledge the helpful criticism of Professor Milton Burton of the University of Notre Dame.

BUFFALO, NEW YORK

---

[11] W. M. Dale, J. V. Davies and W. J. Meredith, *Brit. J. Cancer*, **3**, 31 (1949).

[12] H. Fricke and B. W. Peterson, *Am. J. Roentgenol. Radium Therapy*, **17**, 611 (1927).

[13] J. Weiss, *Nature*, **153**, 748 (1944); **157**, 584 (1946).