alyst. Column 4 shows the amount of pure chromic anhydride which was found experimentally to have the same (initial) activity for aqueous peroxide decomposition as did the given weight of catalyst. The approximate correspondence between the values in columns 3 and 4 indicates that the activities of the oxidized catalysts for this reaction can be largely attributed to the chromic anhydride, or its equivalent, formed on the surfaces of these catalysts during high temperature oxidation.

TABLE II

COMPARISON OF SURFACE OXIDATION AND CHROMIC ANHYDRIDE REQUIRED FOR THE SAME REACTION RATE

(1) Catalyst	(2) Wt. cat., g.	(3) CrO_3 present in cat., mg.	(4) Pure CrO_3 required for same activity, mg.
Oxidized chromia gel	0.10	1.9	4
Oxidized chromia gel	.20	3.8	9
Oxidized chromia gel	.30	5.7	11
Oxidized chromia–alumina (Houdry Type R)	.10	1.8	2
Oxidized chromia–alumina (Houdry Type R)	.20	3.6	4
Oxidized chromia–alumina (Houdry Type R)	.30	5.4	7
Oxidized coppt. chromia-alumina	.05	4.8	6
Oxidized coppt. chromia-alumina	.10	9.6	9
Oxidized coppt. chromia-alumina	.20	19	14

The finite activity of the reduced samples, in spite of their negligible CrO_3 content, is responsible for the fact that the ratio of activities of the oxidized to the reduced samples is less than the ratio of the CrO_3 contents of the same samples.

Experimental

The chromia gel was prepared from dilute solutions of ammonium hydroxide and chromium nitrate, dried in air at 110°, and then stabilized by several cycles of oxygen and hydrogen at 500° (ending with oxygen). The 20% chromia-alumina impregnated catalyst is the Houdry Type R catalyst, which is used for the commercial production of butadiene. The coprecipitated chromia–alumina catalyst was prepared from solutions of sodium aluminate (80 mole per cent.) and chromium acetate (20 mole per cent.) and dried in air at 110° and finally at 500°.[4,5]

The surface areas of the stabilized chromia gel and the 20% chromia–alumina (Houdry Type R) are 35 and 50 $m.^2/g.$, respectively. Coprecipitated chromia–alumina catalysts of the type used in this work have areas several times greater than these.

Each catalyst was pretreated with oxygen or hydrogen at 500° in a flow system and after being cooled in the pretreatment gas to 30° was transferred to a static system. Five cc. of 30% hydrogen peroxide were then added to the catalyst and the rate of reaction determined by measuring the amount of oxygen liberated as a function of time.

When the reaction rate was slow, the liberation of oxygen was followed for about ten minutes. With the more active catalysts the reaction was followed until the liberation of about 50 cc. of oxygen.

The extent of surface oxidation was determined by an iodometric method.[1-3] The titratable acidity was determined by adding standard sodium hydroxide to a weighed amount of catalyst and then, after a given time, titrating with standard hydrochloric acid; the acidity values given in Table I are the extrapolated values at zero time. The *p*H values were determined by suspending 1 g. of catalyst in 10 cc. of distilled water and vigorously stirring the suspension for several hours until a constant *p*H was obtained.

Powdered catalysts were used in all the experimental work reported in this note.

Acknowledgment.—The authors wish to express their appreciation to Dr. G. A. Mills for his constructive criticism of this work and to the Houdry Process Corporation for permission to publish this material.

HOUDRY PROCESS CORPORATION
MARCUS HOOK, PENNSYLVANIA

---

[4] E. Buck and E. C. Hughes, U. S. Patent 2,290,033, July 14, 1942.

[5] E. C. Hughes, U. S. Patent 2,323,868, July 6, 1943.

Temperature Coefficient of the Radiation Induced Oxidation of Ferrous Sulfate[1]

BY HAROLD A. SCHWARZ

RECEIVED NOVEMBER 9, 1953

Three determinations of the temperature coefficient of the radiation induced oxidation of air-saturated ferrous sulfate solutions have appeared. Dewhurst[2] found a coefficient of 0.4% per degree, Hardwick[3] found 0.2% per degree and Minder and Liechte[4] found no dependence but did not state their limits of error.

In the mechanism that is accepted for this reaction[5] the hydrogen atoms, hydroxyl radicals and hydrogen peroxide produced react stoichiometrically with the ferrous ions with no competing steps. Hence any temperature coefficient found should represent a change in the net dissociation of the water.

Experimental

Triply distilled water was used in preparing the solutions.[6] The solutions were 0.001 *M* in ferrous sulfate and sodium chloride (to inhibit any organic effect[7]) and 0.8 *N* in sulfuric acid. All equipment used was cleaned with steam. The irradiation cells were preirradiated with several million roentgen. A water thermostated cylindrical cobalt-60 source[8] was used in the irradiations. All results were corrected to the same time on the basis of a 5.2 year half-life of the source.

Ferric ion was determined spectrophotometrically by direct reading of the absorption of the ferric sulfate complex at 305 mμ on a Beckman DU spectrophotometer,[9] using an extinction coefficient of 2190. Since all optical density measurements were made at room temperature, the effect of change in density of the solution cancels out.

Suitable thermal controls were run with the samples, a portion of the ferrous sulfate solution being kept at the reaction temperature during the irradiation. The amount of oxidation in the blanks was very small, amounting to only 1% of the observed radiation induced reaction at 72°.

Discussion

The results for solutions with chloride ion added are given in Fig. 1. Each point is an average of between 4 and 8 determinations. The temperature coefficient found is 0.04 ± 0.03% per degree,

---

[1] Research carried out under the auspices of the U. S. Atomic Energy Commission.

[2] H. A. Dewhurst, doctoral dissertation, McGill University, Montreal, Que. (1949).

[3] T. J. Hardwick, *Can. J. Chem.*, **31**, 881 (1953).

[4] N. Minder and A. Liechte, *Experientia*, **2**, 410 (1946); see also C. J. Hochanadel and J. A. Ghormley, *J. Chem. Phys.*, **21**, 880 (1953).

[5] F. H. Krenz and H. A. Dewhurst, *ibid.*, **17**, 1337 (1949).

[6] E. R. Johnson and A. O. Allen, THIS JOURNAL, **74**, 4147 (1952).

[7] H. A. Dewhurst, *J. Chem. Phys.*, **19**, 1329 (1951).

[8] H. A. Schwarz and A. O. Allen, *Nucleonics*, in press.

[9] T. J. Hardwick, *Can. J. Chem.*, **30**, 17 (1952).

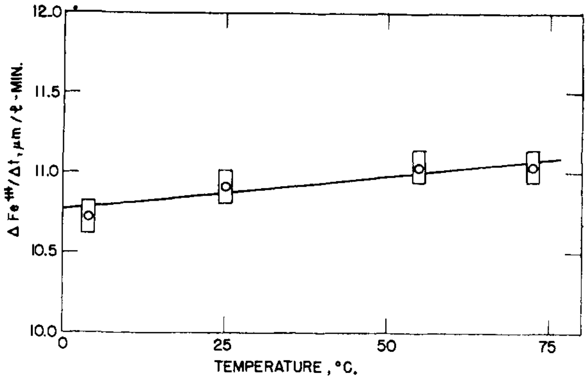

Fig. 1.—Variation of rate of oxidation of ferrous ion with temperature. Rate given as micromoles per liter per minute.

or smaller by a factor of 5 and 10, respectively, than that found by Hardwick and Dewhurst. At 72°, the ferrous oxidation-time curve did not go through the origin. Evidently chloride ion cannot completely protect the reaction from traces of organic matter at this temperature, and the point plotted is the least mean square slope of the line not assuming the origin. If the origin is assumed, this point is raised by 3%.

Some results for solutions without chloride ion are given in Table I. It is to be noted that the ratio of the amount of iron oxidized to the time decreases with time at 50° while the effect is much smaller at 25°. This effect might be expected if small amounts of organic impurities are present. The temperature coefficient of the apparent initial rates is of the order of that obtained by Dewhurst and Hardwick. The least mean square oxidation rate at 50° is 11.1 ± 0.1 while it is 11.0 ± 0.1 at 25°. These values would still represent a maximum rate of oxidation, as the non-linearity of the curve is not considered. However, these values are in good agreement with those obtained in the presence of chloride.

TABLE I

RATIO OF IRON OXIDIZED TO TIME

Irradiation, min.	25°	50°
5	11.3, 11.2	11.8
10	11.2, 11.0	11.7
15	11.3, 11.2	
20	11.0, 11.0	11.4
25	11.0	11.2
30		11.2, 11.3

The temperature dependence, if any, may be due to (a) a change in radiation intensity due to a change in geometry of the source and shielding with temperature although it is hard to see how this could produce an observable effect, or (b) a variation with temperature in the net amount of water decomposition produced by radiation in 0.8 *N* sulfuric acid solutions, or (c) an impurity effect. The amount of impurity necessary to produce this effect is of the order of a few micromoles per liter and thus quite difficult to guard against. In any event, the coefficient is small and need not be considered in comparing results from laboratory to laboratory.

DEPARTMENT OF CHEMISTRY
BROOKHAVEN NATIONAL LABORATORY
LONG ISLAND, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Changes in the Intrinsic Viscosity and Optical Rotation of Bovine Plasma Albumin Associated with Acid Binding[1]

BY JEN TSI YANG AND JOSEPH F. FOSTER

RECEIVED NOVEMBER 2, 1953

Structural changes in bovine plasma albumin in acid solution have been investigated by measurement of intrinsic viscosities and of specific rotations (extrapolated to zero concentration) over the *p*H range 1.3 to 7.0, both with and without added salt. Below *p*H 4 both $-[\alpha]_0$ and $[\eta]_0$ rise to a maximum at *p*H 2.2–2.7 followed by a decrease at lower *p*H. The height of the maximum is markedly depressed by added electrolyte. The viscosity behavior is in all respects analogous to that familiar in the case of synthetic polymeric electrolytes and can be interpreted on the basis of a swelling due to coulombic repulsion. Extrapolation of the data to zero ionic strength yields a monotonic sigmoid curve when either $-[\alpha]_0$ or $[\eta]_0$ is plotted *vs.* *p*H the curve being, however, much steeper than the titration curve. The total increase in $[\eta]_0$ (hydrodynamic volume) is over 10-fold, the increase in $-[\alpha]_0$ approximately 50%. The parallel shift in $-[\alpha]_0$ and $[\eta]_0$ is suggestive of an all-or-none rather than a gradual stepwise expansion of the molecule. The swelling must be essentially isotropic in view of the almost complete absence of streaming birefringence. The reaction is immeasurably fast and completely reversible as judged by (1) the return of both $-[\alpha]_0$ and $[\eta]_0$ to the original values when the *p*H is returned to the isoelectric point, (2) the fact that the results are independent of the sequence in which the reagents, acid and salt, are added and (3) the observation that regenerated protein gives an all-or-none reaction with sodium dodecylbenzenesulfonate which is indistinguishable from that of the native protein.

The titration behavior of proteins with acids and bases has been the object of much investigation. To a first approximation the results in most cases are in agreement with those expected on the basis of the amino acid content, suggesting that the dissociable groups are located on the surface of the protein molecule and are thus readily available for reaction with protons in the surrounding medium. Recently, however, it has become clear that at least in certain cases the situation is not so simple. Steinhardt and Zaiser[2] have shown that there is associated with the acid titration of carbonylhemoglobin

---

[1] Journal Paper Number J-2396 of the Iowa Agricultural Experiment Station, Ames, Iowa. Proj. 1223. This research was carried out under contract Nonr-803 (00) of the Office of Naval Research. Presented before the Division of Biological Chemistry of the American Chemical Society, September, 1953.

[2] J. Steinhardt and E. M. Zaiser, THIS JOURNAL, **73**, 5568 (1951); **75**, 1599 (1953); *J. Biol. Chem.*, **190**, 197 (1951).