entropy values[8] are $\Delta S^* = -43.0$ and $\Delta S_2^* = -13.0$. If these values can be accepted tentatively for the acetyl compound the non-electrostatic contributions are found to be $(\Delta S^*)_{\text{n.e.s.}} = 13$ and $(\Delta S_2^*)_{\text{n.e.s.}} = -13$. The value of -30 for $(\Delta S^*)_{\text{e.s.}}$ suggest that, as with hydrocinnamic ester, there is considerable charge separation during complex formation: this is rather to be expected for an uncharged substrate. There appears to be little further separation during the reaction of the complex. The non-electrostatic entropy values indicate some structural change in this system, the enzyme unfolding during complex formation and folding during the subsequent process.

Experimental

The enzyme, salt-free α-chymotrypsin, was used in solution at a concentration of 8.41×10^{-6} *M*, calculated on the basis of a molecular weight of 27,000.[10] The solvents used were methanol–water mixtures of various concentrations. All water used was triply distilled in an all-glass apparatus. The kinetic procedure was very similar to that employed by Snoke and Neurath,[6] the main difference being that the buffer concentration used was very much lower in the present experiments, a 0.0045 *M* NaOH–NaH_2PO_4 buffer being used. The *p*H optimum was found to be 7.8, and all work was done at this *p*H.

Rates were measured in 15, 20 and 25% methanol–water, and at the two extreme substrate concentrations, 0.00075 *M* and 0.01 *M*. The values of k_2 and k_2K obtained from the intercepts on the two axes are given in Table I. The values of *A* calculated from the plots of log k_2 and log k_2K *vs*. $1/D$, and the corresponding entropies, are also shown in Table I. The dielectric constants were taken from the work of Davies and Jones.[11]

TABLE I

VALUES OF k_2 AND k_2K

% Methanol (by weight)	D	$k_2 \times 10^2$	k_2K
15	72.48	1.84	17.1
20	70.25	1.38	12.5
25	68.01	1.07	6.2
		$A - -1.77 \times 10^5$	-3.38×10^5
		$(\Delta S_2^*)_{\text{e.s.}} = -20$ e.u.	$(\Delta S^*)_{\text{e.s.}} = -38$ e.u.

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[10] E. Jansen, M.D. Fellows-Nutting, R. Jang and A. K. Balls, *J. Biol. Chem.*, **179**, 189 (1949); E. Jansen, M.D. Fellows-Nutting and A. K. Balls, *ibid.*, **179**, 201 (1949).

[11] R. Davies and T. Jones, *Phil. Mag.*, **28**, 307 (1939).

Solubility of Cerium(IV) Pyrophosphate

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The solubility of cerium(IV) pyrophosphate was measured in water and in four sulfuric acid solutions ranging from 0.114 to 0.684 *N*. Phosphorus-32[2] was used to trace the cerium(IV) pyrophosphate. The results are given in Table I.

The solubility increases linearly with sulfuric acid concentration in the region 0.114 to 0.342 *N* acid. Cerium(IV) pyrophosphate has a greater solubility in sulfuric acid than the analogous thorium pyrophosphate[3] has in hydrochloric acid solutions of similar normalities. An examination of our data plus data of Moeller and Schweitzer[3] also indicates that cerium(IV) pyrophosphate is more soluble in hydrochloric acid solutions than in the same normality sulfuric acid solutions by about a factor of two.

TABLE I

Acid concn., *N*	Average c./min.	CeP_2O_7, g./liter	CeP_2O_7, moles/l. × 10^4	ThP_2O_7,[3] moles/l. × 10^4
H_2O	4.5	0.00007 ± 0.00005	0.002	...
0.114	1,740	.026 ± .005	0.8	0.2
.228	3,090	.046 ± .005	1.5	.4
.342	4,950	.073 ± .005	2.3	.6
.684	14,000	.207 ± .010	6.6	...
Standard	9,610			

Experimental

Labeled cerium(IV) pyrophosphate was prepared by reaction of a solution of cerium(IV) ammonium sulfate with an excess of labeled sodium pyrophosphate solution, allowing the precipitate to digest overnight and washing the filtered precipitate thoroughly with warm water and hot ethyl alcohol. The resulting precipitate was a light yellow powder of very fine grain. The labeled sodium pyrophosphate was prepared by heating 4 g. of disodium phosphate with a trace of phosphoric acid containing 400 microcuries of phosphorus-32 in a furnace at 450° for two hours.

The labeled sodium pyrophosphate solution was standardized[3] by treating an excess with a standard solution of thorium nitrate. Thorium pyrophosphate is quantitatively precipitated[3,4] and the activity of the supernatant liquid was measured; 2.521 milligrams of Th^{+4} in 50 ml. precipitated 48.1% of the original pyrophosphate activity. From the decrease in the activity of the sodium pyrophosphate solution and the known amount of thorium nitrate added, the pyrophosphate concentration of the standard solution is calculated to be 3.927 mg. of $P_2O_7^{-4}$ per 50 ml.

The labeled cerium(IV) pyrophosphate was divided among five 50-ml. volumetric flasks containing various amounts of sulfuric acid (Table I). The flasks were shaken regularly for 72 hours in a bath maintained at 25.0°. The supernatant liquids were filtered and the radioactivity of each determined in a glass-jacketed Geiger counter tube with a conventional amplifying and scaling circuit. The standard pyrophosphate solution was counted in a similar manner.

Calculation

$$CeP_2O_7\ (\text{g./liter}) = \text{concn. of std. } (78.54 \times 10^{-3}\text{ g. of } P_2O_7^{-4}/\text{liter})(1.81)\left(\frac{\text{c./min. of unknown}}{\text{c./min. of std.}}\right)$$

1.81 = factor converting pyrophosphate into CeP_2O_7

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[1] (a) Linde Air Products Company, Tonawanda, New York; (b) Argonne National Laboratory, Chicago, Illinois.

[2] Tracer supplied by Oak Ridge National Laboratory.

[3] From data of Moeller and Schweitzer, *Anal. Chem.*, **20**, 1201 (1948); their solubility data were determined in HCl.

[4] R. J. Carney and E. D. Campbell, THIS JOURNAL, **36**, 1134 (1914).

On the Production of Electronically Excited Molecules in the Oxidation Products of Graphite

BY R. H. BUSSO

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The determination of hydrocarbon and carbon monoxide flame temperatures has revealed the existence of a latent energy in the combustion products. These products are also the center of an after-burning.