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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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.

TABLE I

Acid concn., N	Average c./min.	CeP_2O_7, g./liter	CeP_2O_7, moles/l. $\times 10^4$	ThP_2O_7,[3] moles/l. $\times 10^4$
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			

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.

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).

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

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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.

Light emission spectral studies (visible or near ultraviolet) have, for a number of years led investigators to consider that a large part of this light emission is due not to thermal causes but to chemiluminescent reaction products.[1a]

For a number of years systematic investigations of the emission of large quanta of energy by chemical reactions have been carried out in the laboratory of Professor Audubert.[1b] These studies have revealed the role played by high activation energies. It has therefore seemed useful to give an idea of some of the results obtained for carbon combustion since they have sometimes escaped the notice of American publications. These results have been obtained using copper iodide photon counters which are very sensitive in the 1,900 to 2,800 Å. wave length region.[2] It has been shown that the gases leaving the zone of strong reaction surrounding the pure graphite filament (burning at 1773°K. in a rapid stream of low pressure oxygen or air one to 25 cm.) contain carbon dioxide and carbon monoxide electronically excited metastable molecules.[3]

If θ is the apparent mean lifetime ($1/\theta = (1/\tau) + kp$ where τ is the real mean lifetime, p the pressure, k the kinetic constant of deactivation by collision with non-activated molecules), then the form of the curve of variation of $1/\theta$ as a function of pressure shows that these two molecular species can exist in different pressure ranges. At air pressure lower than 2 cm. there are only metastable excited CO molecules whereas at pressure greater than 3 cm. metastable activated CO_2 molecules are present under certain conditions. This identification was made by means of rapid condensation (in liquid air) or through the influence of CO combustion inhibitors (CCl_4 in a proportion of 2%).[4]

A recent preliminary spectral investigation between 1,900 and 2,800 Å. has shown that in the reaction zone (where solid–gas reactions and homogeneous gas reactions occur) surrounding the filament there is emission of bands due to highly activated OH radicals (2,600–2,680 Å.) and of a series of other bands extending almost to 1,900 Å. some of which are due to O_2 and others to CO. It has not yet been possible, however to specify which bands should be attributed to the transitions O_2 (${}^3\Sigma u^- \rightarrow {}^3\Sigma g^-$), CO($A^1\Sigma \rightarrow X^1\Sigma$), CO($a^3\Pi \rightarrow X^1\Sigma$). The Cameron bands are probably present, but with very low intensity because they correspond to partially forbidden transition. All these bands are superposed on a continuous background which seems to extend to 1,900 Å. and can be attributed to the recombination processes $O^1D + O^3P$ and CO $a^3\Pi + O^3P$.

As for the metastable molecules whose lifetime we have determined it is thought that at low pressures where deactivation is less important, CO $a^3\Pi$ molecules are observed which either emit the partially forbidden bands or go over to the CO $A^1\Pi$ level through collision with another molecule, subsequently falling to the ground state with emission of light. In the same way activated CO_2 in the ${}^3\Pi$ state[5] falls to the ground state with emission of forbidden band or else transfers its activation energy to O_2 ${}^3\Sigma g^-$ (emission in the infrared) by formation of a CO_2–O_2 transition complex.[6]

The very small concentrations (10^{-13}) have prevented even qualitative spectral determinations of the above mentioned metastable molecules from being carried out.

One particular point should be made. In the 1,900–2,000 Å. region there is particularly intense emission. It should be noted that the excited levels CO and O_2 are energetically very close to each other and so transfer of energy by resonance is consequently facilitated.

The experimental demonstration of the existence of very high quanta in relatively large amounts in the combustion processes gives them an importance which has been denied to chemiluminescent processes. The investigations of Gaydon, *et al.*,[7] our investigations and those of Laidler seem to imply that highly excited molecules play an important role in the energy chain which occurs in chain reactions or in their initiation. However, as we have attempted, an explanation remains to be found for the origin of these molecular excitation energies some of which exceed 150 kcal. in the case of carbon combustion.

In conclusion it can be said that the results which we have obtained for carbon oxidation (together with those of Whittingham in another wave length)[8] demonstrate that there is a close analogy with the phenomena accompanying flame combustions: identity of active free radicals, presence of large quanta of energy, etc. The following schemes summarize our results.

$$\left.\begin{matrix}\text{C* (active centers)}\\ \text{C}\end{matrix}\right\} + \left\{\begin{matrix}O_2{}^3\Sigma g^-\\ O_2{}^3\Sigma u^-\end{matrix}\right\} \longrightarrow \left\{\begin{matrix}\text{CO}\\ \text{CO*}\\ \text{CO* metastable}\end{matrix}\right.$$

$$\text{CO*} \longrightarrow \text{CO} + h\nu' \text{ (4th positive)}$$

$$\text{CO*met}' \longrightarrow \text{CO} + h\nu'$$

$$\text{CO}^* \xrightarrow{*} O_2{}^3\Sigma g^- \longrightarrow O_2{}^3\Sigma u^-$$

$$O^1D + O^3P \longrightarrow O_2{}^3\Sigma u^- \text{ (continuum)}$$

$$\text{CO} + \left.\begin{matrix}O^1D\\ O^3P\end{matrix}\right\} \longrightarrow \left\{\begin{matrix}CO_2 \text{ (continuum)}\\ CO_2{}^*\\ CO_2{}^* \text{ metastable}\end{matrix}\right.$$

$$CO_2{}^* \longrightarrow CO_2 + h\nu'' \text{ (bands of Gaydon)}$$

$$CO_2{}^*\text{met} \longrightarrow CO_2 + h\nu'''$$

$$CO_2{}^* + O_2{}^3\Sigma g^- \longrightarrow CO_2 + O_2{}^3\Sigma u^-$$

$$O_2{}^3\Sigma u^- \longrightarrow O_2{}^3\Sigma g^- + h\nu'''' \text{ (Schumann–Runge)}$$

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