

CXXXIX.—*Catalysis in the Hydrolysis of Esters by Infra-red Radiation.*

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ACCORDING to the quantum radiation hypothesis of chemical and physical actions as developed by Trautz, Lewis, and Perrin (compare *Ann. Physique*, 1919, [ix], 11, 5), molecules only become reactive after absorption of a definite amount of energy, the critical energy increment, although it appears probable that for

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different reactions the degree of activation necessary may differ, yet these various stages of activation, corresponding with various critical energy increments, are related to one another in a simple manner. This energy acquired by the molecule is potential, and is assumed to be supplied by radiation; thus all reactions, in the broad sense of the term, are photochemical or photophysical. The chemical and physical effects produced by  $\alpha$ -particles and electrons may be included, since the characteristics of photochemical reactions may be quantitatively interpreted with the greatest facility on a corpuscular theory of radiation.

Up to the present time, with the exception of the photochemical reactions taking place in the actinic part of the spectrum, there has been no direct proof of the validity of the extension of this hypothesis into the other parts of the spectrum, especially the infra-red, the arguments in favour of such an hypothesis being indirect, based on experimental data, such as the temperature-coefficient of chemical and physical reactions, the heats of formation of chemical compounds, or the latent heat of evaporation of the elements.

The temperature-coefficient of methyl acetate has been studied in detail by Lamble and Lewis (T., 1914, **105**, 2330), who found that the critical energy increment was about 17,000 calories per gram-molecule, which, on the quantum theory, would be provided by light of frequency of  $\nu = 1.6 \times 10^{14}$ , or wave-length  $\lambda = 1.9 \mu$  in the infra-red portion of the spectrum.

In a constant temperature enclosure, such as a thermostat, the density of the activating radiation,  $u_v$ , is constant, and the most convenient method of causing an alteration in  $u_v$ , and therefore of the reaction-velocity, is by alteration of the temperature.  $u_v$  can, however, be altered by either decreasing or increasing the absorbable radiation density without altering the mean temperature. Thus plants which are photosensitive to the actinic part of the spectrum practically cease growing in the dark, although maintained at the same temperature, and other typical photochemical and photocatalytic reactions behave in like manner. In the case of infra-red radiation, however, it is difficult to shield any part of the reacting system from radiation of any particular absorbable frequency, since the system itself can emit this radiation either as a result of intramolecular vibration or even intermolecular collisions (see Nernst, "Die Theoretischen und Exp. Grundlagen des neuen Wärmesatzes," Halle, 1918, p. 63). Alteration of the medium in which the reacting molecules are dispersed does, however, produce an alteration in the reaction velocity, but, as pointed out above, it is at present uncertain whether this is the result of

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an alteration in  $u_\nu$ , the activating radiation density, or due to an alteration in  $\nu$  equivalent to an alteration in the activating radiation frequencies and the mechanism of the reaction, or to both factors.

It is, however, quite possible to increase the density of the activating radiation,  $\nu$ , by illumination with radiation of the correct wave-length,  $\lambda = 1.9 \mu$ . In the course of time, this radiation will be absorbed, and the energy will be equally distributed over the whole spectrum, resulting in an elevation of temperature, but if the reaction is truly photochemical and selectively absorbs radiation of this frequency, a marked acceleration in the reaction-velocity should result without an appreciable rise in temperature.

To test this point, a series of preliminary experiments was conducted on the rate of hydrolysis of methyl acetate dissolved in dilute hydrochloric acid and exposed to infra-red radiation; the velocity-coefficients obtained in this way were compared with the normal values obtained from identical solutions maintained in the dark.

## EXPERIMENTAL.

As a source of infra-red radiation, preliminary experiments indicated that an arc lamp was unsuitable, since, although the carbon spectrum lines could be maintained at fairly uniform intensity, the infra-red portion of the spectrum (produced by the hot vapours) fluctuated in intensity. A uniform, although relatively feeble, infra-red beam was obtained from a small bundle of the oxide filaments commonly employed in the Nernst glow-lamp. A number of experiments were likewise conducted with a nichrome spiral raised to  $600^\circ$ ; the relatively large quantity of non-radiant heat proved, however, to be a serious disadvantage. The sun was found to be the most convenient source of suitable radiation. In all cases, the spectrum was obtained by dispersion through a simple optical system of lenses and quartz prism, a salt prism not being available. No attempt was made to select any narrow spectral beam, but that part of the spectrum was employed commencing with the portion of the red just beyond the visible and stretching to an indefinite extent into the infra-red. To eliminate as far as possible the material absorption of the radiation, and thus minimise the dissipation of the energy as heat, the methyl acetate was illuminated directly with the radiation without the intervention of any glass. The solution undergoing hydrolysis was contained in a 100 c.c. beaker covered on the outside with tinfoil, a similar beaker containing the control solution.

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Both beakers were maintained at uniform temperature by immersion in a thermostat or in broken ice and water. The temperature of each solution was continually observed, and samples for analysis withdrawn at simultaneous intervals for titration with 0.054*N*-baryta. In all respects, except for illumination, both solutions were maintained under identical conditions and treated in the same manner.

In the following tables are given the data of a number of experiments and the velocity-coefficients therefrom.

## Illuminant: Nernst Filaments.

Acid: 0.1987*N*-HCl. *k* calculated as a unimolecular constant.

## (I.)

Time.		Control.		<i>k</i> × 10 <sup>4</sup> .	Illuminated.		<i>k</i> × 10 <sup>4</sup> .
Hrs.	Min-utes.	Tempera-ture.	Titre. C.c.		Tempera-ture.	Titre. C.c.	
1	55	21.75°	7.36	—	21.75°	7.36	—
2	9	—	7.50	12.71	—	7.76	36.79
2	39	21.75	8.22	23.16	21.80	8.54	36.81
3	4	—	8.34	22.46	—	8.64	25.77
4	15	21.75	8.80	14.10	21.80	8.83	14.39
5	25	—	9.48	15.07	—	9.50	15.24
α	—	—	15.19	—	—	15.19	—

## (II.)

12	46	20.9°	7.30	—	21.1°	7.20 (?)	26.00
12	58	22.3	7.34	7.39	22.3	7.45	31.67
1	14	23.4	7.37	6.00	23.7	7.65	41.35
1	31	23.7	7.45	9.26	23.85	8.00	41.09
1	46	24.9	8.01	25.22	24.7	8.38	41.69
(Time 2 hrs. 4 mins.)							
2	14	24.5	8.16	26.54	24.2	8.57	—
3	10	18.35	8.51	24.27	18.2	9.10	40.15
4	45	18.35	9.84 (?)	41.94	17.9	9.55	41.94
α	—	—	11.40	—	—	11.40	—

## (III.)

Time.		Titre. C.c.		Temperature.		<i>k</i> × 10 <sup>4</sup> .	
Hrs.	Min-utes.	Control.	Illum-inated.	Control.	Illum-inated.	Control.	Illum-inated.
9	35	6.09	6.09	21.70°	21.70°	—	Dark.
9	49	6.26	6.25	21.70	21.70	19.66	19.66
10	7	6.50	6.57	21.30	21.30	20.04	26.22
10	49	7.08	7.38	21.20	21.25	22.99	30.83
11	49	7.31	7.67	20.75	20.75	16.42	18.21
1	0	8.46	8.79	20.75	20.80	23.39	27.78
α	—	12.21	12.21	20.75	20.75	—	—

Illuminant: Sunlight.

Time.		Temperature.		Titre. C.c.		$k \times 10^4$ .		Remarks.
Hrs.	Min-utes.	Con-trol.	Illum-inated.	Con-trol.	Illum-inated.	Con-trol.	Illum-inated.	
1	28	1.0°	1.0°	7.20	7.20	—	—	—
1	39	0.5	0.5	7.22	7.23	4.99	8.47	—
1	51	0.0	0.0	7.23	7.25	4.46	5.82	—
2	3	0.0	0.0	7.26	7.30	4.39	6.85	—
2	13	0.0	0.0	7.28	7.31	4.34	6.28	Sun clouded.
2	29	0.0	0.0	7.30	7.35	4.23	6.26	—
2	51	1.0	1.0	7.34	7.38	4.34	5.75	Sun clouded.
3	52	4.0	4.0	7.48	7.54	4.39	5.47	—
$\infty$		—	—	11.06	11.06	—	—	—

Illuminant: Sunlight and Nichrome Coil.

Time.		Temperature.			Titre. C.c.		
Hrs.	Min-utes.	Control.	Sun.	Nichrome.	Control.	Sun.	Nichrome.
1	50	4.0°	4.0°	14.0°	7.10	7.10	7.10
2	3	2.0	4.0	11.0	7.13	7.15	7.17
2	12	1.5	2.5	11.5	7.18	7.28	7.35
2	23	1.5	2.5	11.0	7.23	7.28	7.37
2	53	1.5	2.5	11.0	7.25	7.30	7.62
3	14	1.5	2.5	11.0	7.25	7.30	7.67
6	9	1.5	2.5	11.0	7.70	7.81	8.49
$\infty$		—	—	—	13.29	13.29	13.29

Time.		$k \times 10^4$ .			Nichrome calculated on temperature basis.
Hrs.	Min-utes.	Control.	Sun.	Nichrome.	
1	50	3.84	—	—	—
2	3	4.89	12.21	18.97	9.02
2	12	4.93	12.29	18.49	12.23
2	23	3.80	7.41	13.48	11.90
2	53	2.37	5.34	13.82	9.19
3	14	4.05	3.34	9.61	5.73
6	9	—	4.85	10.12	5.27

It is evident that the illuminated methyl acetate is hydrolysed much more rapidly than that maintained at the same temperature in the dark.

That the variability in the velocity-coefficient of the illuminated reactants is chiefly due to an alteration in the intensity of the infra-red radiation was evident from the obvious alteration in the intensity of the sunlight by the passage of clouds. To control this factor, experiments were conducted in which the rate of liberation of iodine by catalytic atmospheric oxidation from acidified potassium iodide was simultaneously measured. This reaction is a typical photochemical one. It is evident from the following figures that the same factor, namely, the radiation intensity, affects both reactions, an alteration in the velocity-coefficient of one reaction coinciding approximately with a similar alteration in the other.

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Illuminant: Sun.

Time.		Titre. C.c.		Temperature.		$k \times 10^4$ .		Milligram of iodine liberated per minute.	Remarks.
Hrs.	Mins.	Control.	Illuminated.	Control.	Illuminated.	Control.	Illuminated.		
1	38	5.90	5.90	9.0	9.0	3.32	3.32	—	Both dark.
1	53	5.93	5.93	3.0	3.5	3.33	7.61	0.0053	Both dark.
2	9	5.96	6.03	0.5	0.5	3.66	6.63	0.0023	Illuminated.
2	23	6.00	6.08	0.5	0.5	3.66	5.53	0.0043	—
2	40	6.03	6.10	0.5	0.5	3.36	—	—	—
3	1	6.06	6.16	2.0	2.0	—	5.47	0.0045	—
3	22	6.11	6.20	1.0	1.0	3.47	5.03	0.0026	—
3	41	6.13	6.23	1.0	0.5	3.21	4.48	—	—
$\infty$		9.73	10.90	—	—	—	—	—	—
1	12	5.88	5.82	6.0	9.0	2.78	3.49	—	Dark.
1	26	5.90	5.85	1.0	3.0	2.69	12.90	0.0014	Illuminated.
1	46	5.93	6.05	1.0	1.0	2.48	9.93	0.0036	—
2	2	5.95	6.08	1.0	0.5	3.68	6.51	0.0033	—
2	17	6.02	6.11	1.0	1.0	3.05	6.51	—	—
2	31	6.02	6.10	1.0	1.0	2.94	6.76	0.0164	—
2	46	6.05	6.17	1.0	1.0	—	—	—	—
$\infty$		11.60	11.14	—	—	—	—	—	—

Illuminant: Sun. Temperature, 0°.

Time.		Control.		Illuminated.		Milligram of iodine liberated per minute.
Hrs.	Mins.	Titre.	C.c. $k \times 10^4$ .	Titre.	C.c. $k \times 10^4$ .	
2	35	5.75	1.87	5.75	—	—
2	51	5.77	2.06	5.85	9.92	0.0043
3	8	5.81	3.70	5.86	4.11	0.0025
3	33	5.88	4.36	5.90	4.39	0.0025
3	51	5.95	—	5.97	5.99	0.0030
$\alpha$		11.85	—	11.85	—	—

It seemed possible that the radiation, falling on the surface of the methyl acetate solution, would produce a local rise of temperature, and that the heat would be carried by conduction to the walls of the vessel before the whole body of the solution acquired a higher temperature; thus local rapid hydrolysis might be produced. This possibility was, in reality, remote, since the solution was frequently agitated, and no difference in temperature was observed. Nevertheless, it was thought desirable to test this point experimentally. A small vessel containing oil, which could be maintained at any desired temperature by means of an electric resistance immersed in it, was lowered just under the surface of the methyl acetate solution, and sufficient energy was supplied to the oil to maintain the methyl acetate about 0.5° higher than the control experiment.

The velocity-coefficients obtained in this way agreed very closely with those calculated from the control experiments after correction for a rise in temperature of 0.6°, as is evidenced from the following values:

$k \times 10^4$ observed .....	2.13	3.98	3.73	3.92	3.96
$k \times 10^4$ calculated.....	2.13	3.99	3.73	3.86	3.96

From these experiments, it would seem that the hydrolysis of methyl acetate is in reality accelerated by irradiation in the infra-red portion of the spectrum, an interesting example of infra-red photochemical action; furthermore, that this spectral region is the region of activity anticipated by the application of the activation and quantum theories to chemical change.

It is hoped to continue and extend these experiments in the near future in order, if possible, to elucidate the mechanism of the catalytic activity of the acid employed. There are two tenable theories to explain this catalytic activity, either by an increase in the activating radiation density or by an alteration in the mechanism of the reaction.

Although the above experimental data, limited to one acid concentration, are too limited to draw any definite conclusion, it would appear probable that the second hypothesis, namely, an alteration

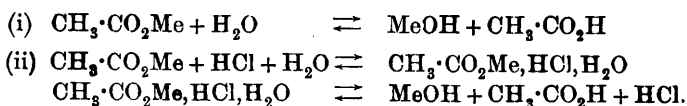
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in the mechanism of the reaction, that is, the intermediate-compound theory of catalysts, is the correct one.

It will be noted that during the first period of illumination there is a very remarkable increase in the velocity-coefficient, and that subsequently the rate of reaction diminishes to a fairly constant value, which is, however, still greater than that of the unilluminated sample.

This phenomenon is not readily intelligible on the assumption of the action of the acid as affecting a simple increase in the radiation density, since a further increase in the radiation density should increase the reaction velocity *pro rata*. On the intermediate-compound theory, however, the observed result is to be anticipated.

Briefly, if the two reactions be represented by the following purely hypothetical equations:



the rate of decomposition in each case being unimolecular in excess of water, then the first reaction-velocity is governed by the rate of activation of the methyl acetate to react with the active water, and the second by two reactions, namely, the rate of activation of the methyl acetate to react with active hydrochloric acid, and by the rate of activation of the complex to break down into the products of the reaction. The rate of any sequent reaction is always governed by the slowest of the intermediate reactions; thus, if we assume the slowest one in this case to be the decomposition of the complex, then illumination with a particular frequency of light will accelerate the decomposition of the complex, so that the reaction-velocity will then be governed by the next slowest reaction, which we have assumed to be the combination of the methyl acetate and hydrated hydrochloric acid. This reaction, however, takes place more rapidly than the combination of methyl acetate and water. On this hypothesis of series reactions, the primary acceleration on illumination is to be attributed to the rapid decomposition of the complex, which is present in relatively large quantities, since it breaks down but slowly; the primary accelerates, then falls off until the normal rate of the next slowest reaction sets in.

### Summary.

Preliminary experiments have indicated that the hydrolysis of methyl acetate is catalytically accelerated by infra-red radiation.



The spectral region of photoactivity is in agreement with that calculated on the activation and quantum theories of chemical action.

The experimental data obtained are most readily interpreted on the intermediate-compounds hypothesis in the case of the hydrolysis of esters by dilute acids. It is proposed to extend these experiments in order to obtain further information as to the number and nature of these intermediate compounds, and to examine the spectral region of their activation in more detail.

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