

Chemistry. — "*Catalysis. IX. Thermal and photochemical reactions*"

By NIL RATAN DHAR. (Communicated by Prof. ERNST COHEN).

(Communicated at the meeting of September 25, 1920).

In a foregoing paper (DHAR, *Trans. Chem. Soc.* 1917 **111**, 707) it was shown that the temperature coefficient of the oxidation of potassium oxalate by iodine has the value 7.2 for a 10° rise in the dark and this reaction is extremely sensitive to light.

It occurred to me that all reactions which have high temperature coefficients should be sensitive to light.

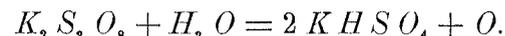
I have shown previously that most uni-molecular reactions have high temperature coefficients and I investigated the effect of tropical sunlight on several of these reactions, and the following results were obtained.

Ammonium nitrite decomposes fairly readily at about 33° in sunlight, whilst at 33° in the dark there is hardly any decomposition. The temperature coefficient for a 10° rise in the dark is about 4.5 (ARNDT, *Zeit. Phys. Chem.* 1901, **39**, 64).

The intramolecular transformation of acetyl chloranilide to par-chloracetanilide has the temperature coefficient 3.2 in the dark. (RIVETT, *Zeit. Phys. Chem.* 1913, **82**, 201) and BLANKSMA (*Rec. trav. Pays.* 1903, **22**, 290) has shown that the change is sensitive to light.

Similarly the pseudo-unimolecular reactions, the hydrolysis of cane sugar and the decomposition of potassium persulphate, are highly influenced by light. An aqueous solution of cane sugar when exposed for several days to tropical sunlight, becomes converted into the invert sugars.

GREEN and MASSON (*Trans. Chem. Soc.* 1910, **97**, 2083) have shown that potassium persulphate is slowly decomposed by water according to the following equation



This reaction has the temperature coefficient 5 in the dark. I found that the reaction is very sensitive to light and the oxygen given off in 24 hours in sunlight is practically equal to that produced in about 15 days in the dark at 27°.

The decompositions of the sulfine bases and the tetraammonium compounds studied by VON HALBAN have high temperature coefficients

and these reactions when investigated would show great sensitiveness to light (*Zeit. Phys. Chem.* 1909, **67**, 129).

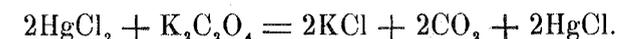
CAIN and NICOLL (*Jour. Chem. Soc.* 1903, **83**, 470) have proved that the decomposition of the diazo salts has the value of about 5 for their temperature coefficients and it is well known that diazo salts are sensitive to light.

PENDLEBURY and SEWARD (*Proc. Roy. Soc.* 1889, **95**, 396) have shown that the reaction between $KClO_3$, KI and HCl has the temperature coefficient of about 4 in the dark and I have found that the reaction is very sensitive to light.

I have already shown (*Trans. Chem. Soc.* 1917, **111**, 707) that the oxidations of sodium formate by mercuric chloride and by iodine has 4.05 for their temperature coefficient. These two reactions are also very sensitive to light (DHAR, *Proc. Akad. Wet. Amsterdam* 1916, **24**, 1324).

I have shown that light markedly accelerates the reaction between iodine and oxalates and now I have tried to find out which part of the spectrum is active in this reaction. For this I exposed five small tubes containing a mixture of potassium oxalate and iodine in a spectrum obtained from a carbon arc-light. It was found that the iodine disappeared first in the tube held in the indigo portion near the violet end of the spectrum. Then that of the tube held in the blue region. The chemical change took place almost simultaneously in the tubes held in the green and violet portions of the spectrum and the colour of the tube in the red end was the last to disappear.

A mixture of mercuric chloride and potassium oxalate undergoes the following change in sunlight:



This decomposition can also be induced by lights obtained from a carbon arc, quartz mercury vapour lamp, and an arc obtained by passing alternating current in electrodes made of thorium and zirconium oxides. I have repeatedly observed that in tropical sunlight, a solution of ammonium cupric oxalate decomposes readily in glass vessels with the separation of metallic copper and evolution of carbon dioxide; but it was found impossible to bring forth this change by light obtained from the carbon arc or the thorium and zirconium oxides arc.

I have found that uranium nitrate markedly accelerates the photo-chemical decomposition of a mixture of mercuric chloride and potassium oxalate, but chromates having the same yellow colour as the

uranium salt exert a markedly negative effect. MATHEWS and WEEKS (Journ. Amer. Chem. Soc. 1917, 39, 635) have shown that uranium nitrate is also a positive catalyst in the photochemical oxidation of sodium sulphite. Moreover, it is wellknown that uranium salts markedly help the photochemical decomposition of organic acids (e.g.), oxalic, formic, lactic etc. Hence it appears that a uranium salt is a positive catalyst of great generality in photochemical reactions.

I have observed that manganese sulphate exerts a negative effect in the photochemical decomposition of a mixture of mercuric chloride and potassium oxalate. It has already been shown that manganese salts act as a negative catalyst in the reactions between phosphorous and chromic acids, formic and chromic acids, mercuric chloride and sodium formate, iodine and sodium formate, silver nitrate and sodium formate, silver nitrate and ferrousammonium sulphate, etc. So it seems that a manganese salt is a negative catalyst for light and dark reactions alike.

I have also observed the effects of the different parts of the spectrum on several other photochemical reactions by passing ordinary sunlight through different solutions and exposing the reacting substances to the filtered lights thus obtained and the results obtained are summarised below:

- | | |
|---|---|
| (1) $\text{HgCl}_2 + (\text{NH}_4)_2\text{C}_2\text{O}_4 \rightarrow$ | } Blue, violet and ultra-violet more active than the red and infra-red. |
| (2) $\text{I}_2 + (\text{NH}_4)_2\text{C}_2\text{O}_4 \rightarrow$ | |
| (3) $\text{FeCl}_3 + (\text{NH}_4)_2\text{C}_2\text{O}_4 \rightarrow$ | |
| (4) Pyrogallol and Pyrogallate
$+ \text{O}_2 \rightarrow$ | } practically uniform acceleration in different parts |
| (5) Hydroquinone $+ \text{O}_2 \rightarrow$ | |
| (6) Cu_2Cl_2 (ammoniacal or acid)
$+ \text{O}_2 \rightarrow$ | |
| (7) Decomposition of $\text{H}_2\text{S} \rightarrow$ | } Blue and violet slightly more active than the red. |
| (8) Quinine acid sulphate $+ \text{H}_2\text{Cr}_2\text{O}_7 \rightarrow$ | |
| (9) $\text{KMnO}_4 + \text{H}_2\text{C}_2\text{O}_4 \rightarrow$ | } Violet and ultra-violet more active than red. |

In a remarkable article PERRIN (Annales de Physique 1919, t. XI, 1) has enunciated the following hypothesis:

"All chemical reactions are provoked by light radiations. Their velocities are determined by the intensity of the light radiations and depend on temperature to such an extent as the light intensity depends on temperature". By applying the idea of the emissive power of perfectly black bodies and its relation to temperature,

PERRIN has deduced the following equation connecting the velocity coefficient and the temperature:

$$2.3 d \log_{10} k = \rho v \frac{dT}{T^2}, \text{ where } k = \text{velocity coefficient, } v = \text{wave-}$$

length of the activating radiation and $T = \text{absolute temperature}$. From his calculations, it is seen that the wavelengths which are active in bringing forth the ordinary chemical changes vary from 2.56 to 0.8 microns. It is also seen that a reaction which is highly sensitive to the influence of temperature, has a small value for its activating wavelength, that is, a reaction of this type would be most sensitive to violet and ultraviolet end of the spectrum. From PERRIN'S calculations it is seen that the reaction between $\text{K}_2\text{C}_2\text{O}_4$ and I_2 , which has the high temperature coefficient of 7.2 in the dark, has 0.8 micron for the wavelength of its activating radiation. In other words, this reaction would be most sensitive to light near the red end of the spectrum. But it is experimentally shown that this reaction is not sensitive to the indigo part near the violet end of the spectrum. My own experiments on several photochemical reactions have shown that the blue and violet portions of the spectrum are most active so far as chemical effects are concerned. Although the hypothesis of PERRIN is still of a qualitative nature, it is a highly suggestive one and my experiments give this hypothesis a sort of general support.

I have tried to prove experimentally that reactions, which are most sensitive to the influence of temperature, are also most sensitive to the influence of light. In a foregoing paper, I have advanced the hypothesis that temperature and light affect a chemical change in a similar way. The experimental evidence brought forward in this article, as well as PERRIN'S hypothesis that all chemical changes are induced by radiations, give additional confirmation to my hypothesis regarding the identity of effects of temperature and light on chemical reactions.

Summary:

a. Evidence has been brought forward in support of the view that reactions, having large temperature coefficients, are sensitive to light. Hence for a chemical reaction, sensitiveness to the influence of temperature and sensitiveness to light radiations go hand in hand.

b. The indigo part near the violet end of the spectrum is most active in the reaction between $\text{K}_2\text{C}_2\text{O}_4$ and I_2 ; blue and violet parts more active than the red in the following cases:

$(\text{NH}_4)_2\text{C}_2\text{O}_4 + \text{HgCl}_2$, $(\text{NH}_4)_2\text{C}_2\text{O}_4 + \text{FeCl}_3$, $\text{H}_2\text{C}_2\text{O}_4 + \text{KMnO}_4$
and Quinine bisulphate + $\text{H}_2\text{Cr}_2\text{O}_7$.

c. Uranium salts are general positive catalysts in photochemical reactions, whilst manganese salts are general negative catalysts in light and dark reactions alike.

d. PERRIN's hypothesis that all chemical reactions are induced by radiations support the view that the effects of temperature and of light on chemical reactions are of an identical nature.

e. A solution of ammonium cupric oxalate decomposes with the separation of metallic copper and evolution of CO_2 in tropical sunlight, but not in carbon-arc-light or the zirconium + thorium oxides-arc-light.

*Chemical Laboratory, Muir Central College,
Allahabad, India.*

Chemistry. — "*Catalysis. X. Explanation of some abnormally large and small temperature coefficients*". By NIL RATAN DHAR.
(Communicated by Prof. ERNST COHEN).

(Communicated at the meeting of September 25, 1920).

SKRABAL (Monatsh. 1914, 35, 1157) has shown that the velocity of formation of iodate from iodine and iodide in a mixture of sodium carbonate and sodium bicarbonate solutions has $\frac{k_{t+10}}{k_t} = 45$.

When a similar reaction was effected in sodium acetate solution, the temperature coefficient is 2.

The velocity of decomposition of iodate in a mixture of acetic acid and sodium acetate solution has $\frac{k_{t+10}}{k_t} = 1.34$. The same reaction in a mixture of disodium and monosodium phosphates gives a temperature coefficient 1.26; in a mixture of KF and HF, the temperature coefficient has the value 0.9 to 1.04 and a mixture of sodium sulphate and sodium hydrogen sulphate leads to the value of 0.85.

SKRABAL remarks that the temperature coefficient must necessarily undergo a change when the substances, which affect the time equation, are transformed into complexes. The relationship between the temperature coefficient T of the original reaction and T' , that of the reaction between the complex substances is governed by the formula,

$$T'/T = e^{10/RT(T+10)(mQ_1 + nQ_2 + \dots + xq_1 + yq_2 + \dots)}$$

in which Q and q represent the heat changes of the complex reaction and the sum $(m + n + \dots + x + y + \dots)$ indicates the order of the reaction. This formula indicates that a great variability of T is to be expected from reactions of the higher orders.

In a foregoing paper (Annales de Chimie et de physique 1919, t. XI, 130) I have definitely proved that this conclusion of SKRABAL, which states that the temperature coefficients of polymolecular reactions are, in general, greater than those of unimolecular ones, is not supported by experimental evidence.

SKRABAL investigated these two polymolecular reactions:

