427. *The Kinetics of Photochemical Oxidation with Dichromate: The Oxidation of Glycerol.**

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The kinetics of the photochemical oxidation of glycerol by dichromate under the influence of polychromatic light have been investigated. Particular stress has been laid upon the influence of temperature, addition of acid or of alkali, and also upon the rôle of the simultaneous thermal reaction. Under certain conditions of experiment (high concentration of glycerol), the existence of a *negative temperature coefficient* was established.

A reaction mechanism has been developed, by means of which, on the supposition of a preceding equilibrium, the negative temperature effect can be explained. The hydrolysed dichromate ion must be considered as the photochemically active component. A new calculation of the heat of hydrolysis gave the value −1186 cals./mol., in good agreement with the caloric effect of the temperature-function of the reaction velocity, *viz.* −1210 cals./mol. The reaction mechanism makes it possible to account also for the other results of the kinetic measurements.

In spite of many investigations (Goldberg, *Z. wiss. Phot.*, 1906, **4**, 95; Luther and Forbes, *J. Amer. Chem. Soc.*, 1909, **31**, 770; Forbes *et al.*, *ibid.*, 1923, **45**, 1891; 1932, **54**, 960; 1933, **55**, 588,

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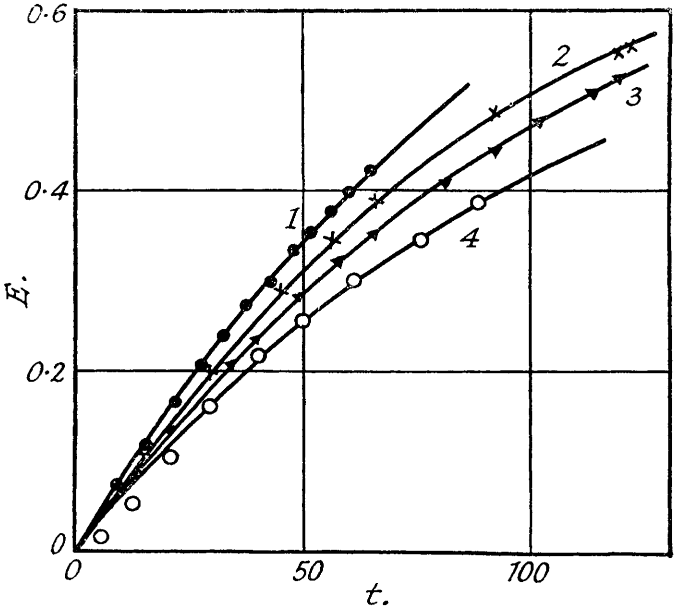
* A short preliminary communication on this subject appeared in *Nature*, 1946, **157**, 373.

2407; Dhar, *J.*, 1923, **123**, 1856; Bowen *et al.*, *J.*, 1927, 2353; 1929, 1648; 1931, 1866; 1932, 2081; Bhattacharya and Dhar, *Z. anorg. Chem.*, 1928, **169**, 381; Morton, *J. Physical Chem.*, 1929, **33**, 1135; Riesenfeld and Hecht, *Z. wiss. Phot.*, 1929, **26**, 369; Winther, *Z. physikal. Chem.*, 1935, *A*, **174**, 41) the oxidations by means of chromates and dichromates have not yet been elucidated in detail. We have now investigated the kinetics of the *photochemical* oxidation of glycerol, laying particular stress on the influence of temperature on the reaction velocity, as it has been found that this reaction, if specific conditions are fulfilled, shows the rather rare phenomenon of a negative temperature coefficient. This has a particular bearing on the elucidation of the reaction mechanism.

EXPERIMENTAL.

The velocity of the photochemical reaction was determined by measuring photoelectrically the extinction of the oxidation product (*i.e.*, the green colour of the tervalent chromium). By exposing the reactants to white light and using appropriate light filters, the measurements could be conducted during the course of the reaction. The light used for the photochemical reaction served also for the photoelectrical measurement of the extinction.

FIG. 1.



$K_2Cr_2O_7$: 5·77 × 10^{-3} *mols./l.* *Glycerol :* 7·51 *mols./l.*

Dependence of reaction velocity on temperature : E = *extinction*, t = *time of reaction in minutes. Curve* 1 *gives the values for* 14°, 2 *for* 25°, 3 *for* 35°, *and* 4 *for* 45°.

The reaction vessel, made of plane parallel glass plates (5 × 5 × 1 cm.), was placed in a thermostat (constant within ±0·1°), and the contents stirred mechanically during exposure to a 500-watt incandescent or to a mercury-vapour high-pressure lamp. Close behind the reaction vessel, screened by a yellow filter, there was a selenium photoelement whose current was measured with a reflection galvanometer.

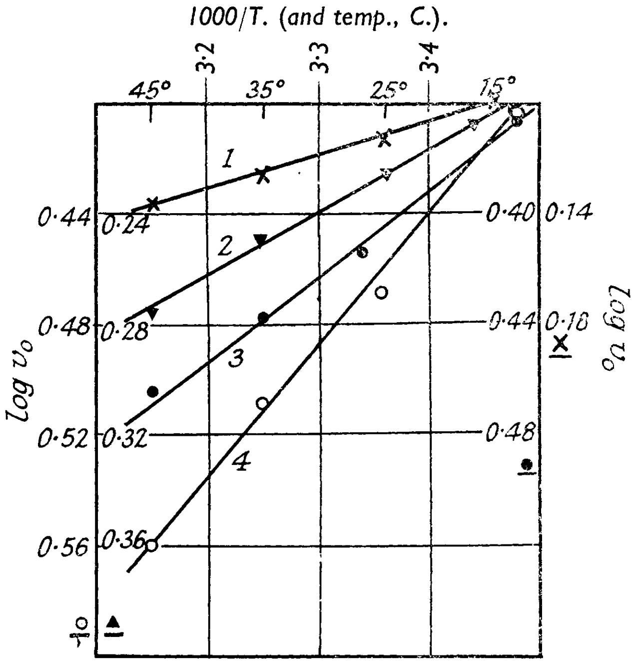
The numerical value of the coefficient of extinction, necessary for the calculation of the velocity of the photochemical reaction, was computed directly from kinetic measurements. As the experiments were conducted with polychromatic light, the *actinometric* determinations gave the " mean " coefficient for the spectral interval that was—in the given experimental arrangement—chemically active. It did not seem necessary to use monochromatic light, as it could be assumed that in the whole spectral interval used for the exposure, the absorption yields the same chemical result. This supposition was eventually confirmed by the results of the experiments.

The reaction velocities were measured with different concentrations of the two components and at temperatures of 14—45°. The influence of the intensity of light on the reaction was also determined.

Fig. 1 shows some of the curves obtained for the velocity. From them a negative temperature coefficient can be inferred. The values of the ordinates of the tangents for the time of 50 minutes have been used as relative values of the initial velocities (v_0).

The results of experiments with a constant concentration of glycerol (7·51 mols./l.) and four different concentrations of dichromate at various temperatures are shown graphically in Fig. 2. The inclination of all straight lines towards the abscissa indicates a negative temperature coefficient (Forster and Blich, *Z. angew. Chem.*, 1910, **23**, 2017; Skrabal, *Monatsh.*, 1912, **33**, 118; *Z. Elektrochem.*, 1915, **21**, 461; Skrabal and Weberitsch, *Ber.*, 1914, **47**, 117; Trautz, *Z. Elektrochem.*, 1915, **21**, 329; Bodenstein, *ibid.*, 1918, **24**, 183; *Z. physikal. Chem.*, 1922, **100**, 68; 1936, **175**, 294; *Helv. Chim. Acta*, 1935, **18**, 743; Padoa, *Gazzetta*, 1921, **51**, I, 3; Schumacher, *Z. physikal. Chem.*, 1927, **129**, 241; *Z. Elektrochem.*, 1929, **35**, 715; Kassel, *J. Physical Chem.*, 1930, **34**, 1777). This coefficient ($Q_{10} = k_{T+10}/k_T$) for the interval between 35° and 45° is 0·91—0·97. It increases as the dichromate concentration increases from $5{\cdot}77 \times 10^{-3}$ to $4{\cdot}62 \times 10^{-2}$ mols./l. With small concentrations of dichromate, the negative temperature coefficient disappears. For a concentration of glycerol of 1·11 mols./l. and a concentration of dichromate of $2{\cdot}31 \times 10^{-2}$ mols./l. we found a temperature quotient $Q_{10} = 1{\cdot}32$. With an increase of temperature the negative temperature coefficient decreases and Q_{10} approaches unity.

Fig. 2.



Cr_2O_7'' = (1) $4{\cdot}62 \times 10^{-2}$, (2) $2{\cdot}31 \times 10^{-2}$, (3) $8{\cdot}09 \times 10^{-3}$, (4) $5{\cdot}77 \times 10^{-3}$, *mols./l.*
Glycerol concentration = 7·51 *mols./l. in all cases.*

From the measured initial velocities v_0, the relative velocity constants k that are independent of changes in concentration can be calculated from the equation

$$v_0 = kI_0(1 - e^{-icp}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

if the absorption constant i is known and if a linear relation between the velocity of reaction and the intensity of light can be supposed. The validity of Beer's law for polychromatic light cannot be assumed without proof; in our case, however, it can be deduced from the experimental material by means of the equation

$$\frac{v_1}{v_2} = \frac{1 - e^{-ic_1}}{1 - e^{-ic_2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where the initial velocities v_1 and v_2 correspond to the concentration of the dichromate c_1 and c_2, while $p = 1$. With the help of this equation we have calculated i by two methods: first, by the development of the series of exponential expressions which give equations that can be solved for i (approximate method); secondly, by transforming equation (2) into

$$v_2 - v_1 = v_2(e^{-c_1})^i - v_1(e^{-c_2})^i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

by means of a graphical method which, after numerical calculation of the expressions within the parentheses, gives i as a function of $v_2 - v_1$. For a number of arbitrarily chosen values for i, curves were obtained that enabled us to read the values for i that correspond to the actual values of $v_2 - v_1$.

Although the values for the absorption coefficient for the different concentrations of potassium dichromate differ appreciably, their mean values are almost identical. This is easy to understand, for it was established by special approximate calculation that the discrepancies in the i values are due, not so much to experimental error, as to inaccuracy of the methods of calculation. The values for the absorption coefficient are almost independent of temperature. The following values were found:

at 25°, $i = 99{\cdot}2$; at 45°, $i = 97{\cdot}2$. The mean value, *i.e.*, $i = 98{\cdot}2$, was used for the calculation of the relative velocity constant according to equation (1).

The linear dependence of the investigated velocity of reaction on the intensity of light is known from the literature, but it follows also from the results of our experiments, since equation (1) is established as valid. It is confirmed also by experiments conducted with the high intensities of the light of the mercury high-pressure lamp.

The velocity constants (k) calculated from the initial velocities by means of equation (1) are given in Table I ($I_0 = 100$). It is clear that the k values obtained for the same temperature agree well with each other independently of the concentration of potassium dichromate.

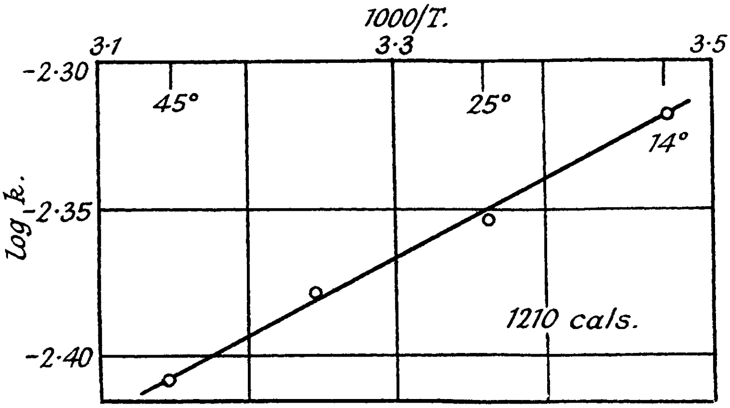
TABLE I.

Concentration of glycerol : 7·51 mols./l.

$K_2Cr_2O_7$, mols./l. × 10^3.	$k \times 10^3$.			
	14°.	25°.	35°.	45°.
5·77	5·09	4·74	4·23	3·84
8·09	4·93	4·31	4·19	4·09
23·1	4·29	3·90	3·79	3·48
46·2	4·92	4·76	4·53	4·25
Mean values	4·80	4·42	4·18	3·91

Fig. 3 shows the graphical evaluation of the temperature function of the velocity constant k according to the Arrhenius equation. The inclination of the straight line corresponds to an energy content of 1210 cals.

FIG. 3.



As the velocity of the concurrent thermal reaction is small, no account was taken of it during the photochemical measurements. The velocities of the reaction in the dark and in the light show a ratio of about 1 : 28 (see Fig. 4).

Addition of an acid (*e.g.*, hydrochloric) increases the velocity of the photochemical reaction but slightly. The increase is linear with the concentration of the acid. The thermal reaction, however, is accelerated considerably by the addition of acid : addition of $4{\cdot}62 \times 10^{-2}$M-hydrochloric acid increases the amount of the reaction products about 16-fold. In a decidedly acid medium the mechanism of the reaction takes a very complicated course.

Addition of alkali (sodium hydroxide) diminishes the velocity both of the thermal and of the photochemical reaction considerably. Solution of potassium chromate are therefore decidedly less photoactive than are analogous solutions of potassium dichromate (see Fig. 5). By means of experiments, the results of which are shown in Table II, we have investigated the quantitative influence of the concentration of hydroxyl ions on the velocity of the reaction. In the table, v denotes the experimentally obtained values for the velocity of the reaction at the start, and $I_{abs.}$ the % of light absorbed with regard to the concentration of the dichromate ions. Their concentration as well as that of $HCrO_4'$ ions has been calculated with the help of the hydrolytic and dissociation equilibrium constants for the Cr_2O_7'' ions and $HCrO_4'$ ions respectively. (The numerical values of those constants are discussed later.) From the reaction mechanism, as set forth in the present paper, the following equation for the influence of the concentration of hydroxyl ions can be deduced :

$$v = k'I_{abs.}/(k'' - [HCrO_4'][OH']) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

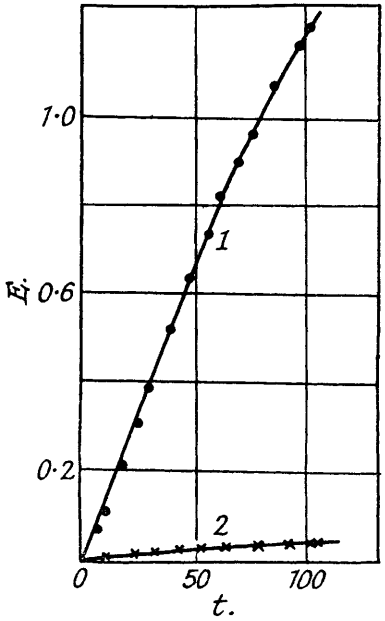
From our experimental data we have calculated the numerical values for k' and k''. The values obtained are also shown in Table II. As the values for k' and k'' are fairly constant, we infer that the above equation is valid, at least in principle. This statement further emphasises the intrinsic validity of the reaction mechanism discussed.

TABLE II.

$[K_2Cr_2O_7] = 2{\cdot}31 \times 10^{-2}$ mols./l.; [glycerol] = 7·51 mols./l.

[OH′].	[HCrO$_4$′].	[Cr$_2$O$_7$″].	*v*.	$I_{abs.}$.	$k' \times 10^{12}$.	$k'' \times 10^{10}$.
$4{\cdot}78 \times 10^{-10}$	$2{\cdot}14 \times 10^{-2}$	$1{\cdot}20 \times 10^{-2}$	0·606	69·23	5·39	6·25
					4·76	5·55
$7{\cdot}60 \times 10^{-9}$	$1{\cdot}94 \times 10^{-2}$	$7{\cdot}55 \times 10^{-3}$	0·590	52·36	4·54	5·62
					5·02	5·66
$4{\cdot}57 \times 10^{-8}$	$9{\cdot}28 \times 10^{-3}$	$1{\cdot}72 \times 10^{-3}$	0·570	15·54	4·58	5·49
					4·63	5·63
$1{\cdot}00 \times 10^{-7}$	$5{\cdot}08 \times 10^{-3}$	$5{\cdot}20 \times 10^{-4}$	0·523	6·23	4·70	5·65
					5·40	5·72
$2{\cdot}63 \times 10^{-7}$	$2{\cdot}10 \times 10^{-3}$	$1{\cdot}25 \times 10^{-4}$	0·432	1·22	5·21	5·67
					4·90	5·66

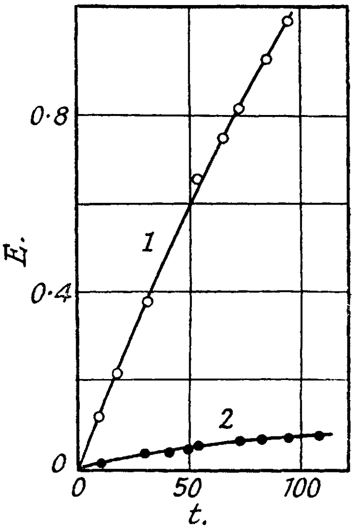
FIG. 4.



$K_2Cr_2O_7$: $2{\cdot}31 \times 10^{-2}$ *mols./l.* *Glycerol*: 7·51 *mols./l.*

(1) *Thermal and photochemical reactions.*
(2) *Thermal reaction only.*

FIG. 5.

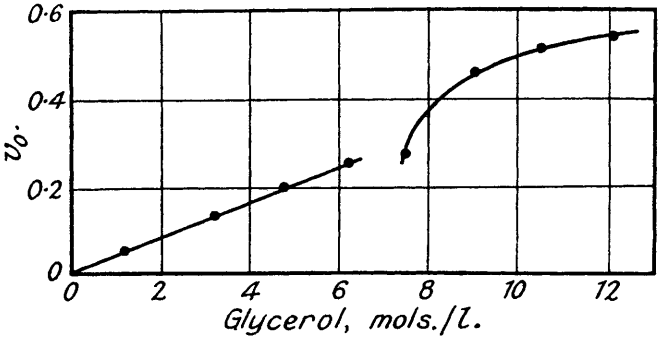


Glycerol: 7·51 *mols./l.*

(1) *Photo-reaction with* $K_2Cr_2O_7 = 2{\cdot}31 \times 10^{-2}$ *mols./l.*
(2) *Photo-reaction with* $K_2CrO_4 = 4{\cdot}62 \times 10^{-2}$ *mols./l.*

The influence of the concentration of glycerol on the velocity of the photochemical reaction has also been studied, and two concentration ranges of glycerol can be distinguished with regard to the velocity of the reaction. In the lower range (up to 6M) the increase of the initial velocity of the reaction is linear with increase of the concentration of glycerol. In the higher range (7—12M) this phenomenon is no

FIG. 6.



$K_2Cr_2O_7$: $5{\cdot}77 \times 10^{-3}$ *mols./l.*

longer observed. Fig. 6 shows the results of measurements with $5{\cdot}77 \times 10^{-3}$M-dichromate, and analogous results have been obtained with concentrations of $2{\cdot}31 \times 10^{-2}$M. The non-linear curve in Fig. 6 can be expressed by the equation

$$v = 0{\cdot}6[C_3H_5(OH)_3]/\{0{\cdot}45 + [C_3H_5(OH)_3]\}$$

The values for the velocity of reaction at the start in Table III have been calculated by means of the above equation. The agreement between the found and the calculated values establishes the validity of the above equation, which has been inferred from the proposed reaction mechanism.

TABLE III.

$[C_3H_5(OH)_3]$, M.	v, found.	v, calc.
0·25	0·28	0·21
1·75	0·45	0·48
3·25	0·51	0·53
4·85	0·54	0·55

The Reaction Mechanism.—From the foregoing kinetic measurements and also from the fact that the photochemical oxidation of glycerol with dichromate shows a negative temperature coefficient it is possible to draw certain conclusions on the reaction mechanism. The few known cases of a negative temperature coefficient have been explained by assuming a chemical equilibrium that *precedes* the reaction determining the velocity. This equilibrium shifts with a rise of temperature in such a way that the concentration of one of the reagents *diminishes*, with resulting decrease of the reaction velocity. It can be easily seen that with such a reaction mechanism a negative temperature coefficient can be the more easily reached the *more* the preceding equilibrium is dependent on the temperature and the *less* this is the case with the reaction itself.

The velocity of *photochemical* reactions is, in general, almost independent of temperature, as the activation energy is furnished, at least for the greater part, by the absorption of the light. It must therefore be inferred that in photochemical reactions a negative temperature coefficient would be expected oftener than is actually the case if only reactions could be found where the preceding equilibrium showed the above-described dependence on temperature.

If we suppose that potassium dichromate, being a strong electrolyte, is completely dissociated in aqueous solution, we have for such solutions the following equations for its hydrolysis and dissociation :

$$(1)\quad Cr_2O_7'' + H_2O \rightleftarrows 2HCrO_4' \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (K_1)$$

$$(2)\quad HCrO_4' \rightleftarrows CrO_4'' + H^{\cdot} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (K_2)$$

$$(3)\quad HCr_2O_7' \rightleftarrows Cr_2O_7'' + H^{\cdot}$$

In neutral or weakly acid solution the equilibrium (3) is shifted strongly towards the right (compare the value of the dissociation constant given by Bowen and Jarnold, *J.*, **1929**, **1648**) so that in those solutions only equations (1) and (2) determine the concentration of the ions. The question arises : which of the equilibria precedes the photoreaction and which ion can therefore be considered as the photoactive component of the reaction ?

We suppose now that equation (1), *i.e.*, the hydrolysis of the dichromate ion, precedes the photoreaction and that the ion Cr_2O_7'' represents the photoactive component. In order to prove this supposition we shall compare the heat of reaction of this hydrolysis equilibrium with the value calculated according to the Arrhenius formula from the influence on the photo-oxidation of glycerol.

The heat of reaction of the equilibrium (1) has not been determined; it has, however, been calculated by LaMer and Read (*J. Amer. Chem. Soc.*, 1930, **52**, 3098) from their measurements of the heat of neutralisation of sodium dichromate by sodium hydroxide to be −13,640 cals./mol. In this calculation, the value of the equilibrium constant (1) to be used is important. The equilibrium constants in (1) and (2), *viz.*, $K_1 = [HCrO_4']^2/[Cr_2O_7'']$ and $K_2 = [H^{\cdot}][CrO_4'']/[HCrO_4']$ have been determined by various authors, but the values obtained differ considerably as can be seen from Table IV.

TABLE IV.

Temp.	K_1.	$K_2 \times 10^7$.	Authors.
25°	0·013—0·04	7·4—8·4	Sherrill [1]
18	—	6·0	Sherrill [1]
25	2·5	—	Beck and Stegmüller [2]
18	—	3·7	Beck and Stegmüller [2]
25	0·044—0·054	—	Stokes *et al.*[3]

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[1] *J. Amer. Chem. Soc.*, 1907, **29**, 1641.

[2] *Arb. Kais. Gesundh.*, 1910, **34**, 446.

[3] *Trans. Faraday Soc.*, 1941, **37**, 566.

LaMer and Read used the mean value of Sherrill's determinations, $K_1 = 0{\cdot}019$. This value is decidedly too low, as can be inferred from the fact that they obtained for the heat of dissociation of the hydrochromate ion, *i.e.*, for the equilibrium (2), a value of +780 cals./mol., which differs even in sign from the value calculated directly from the reaction isochore for the value of the dissociation constant (K_2) for various temperatures, *viz.*, −6772 cals./mol. On the other hand, the value for K_1 given by Beck and Stegmüller cannot be right either, because with it LaMer and Read's measurements cannot be interpreted at all. We have therefore used for our calculations a value of K_1 that is a mean of the data given by Stokes *et al.*, *viz.*, $K_1 = 0{\cdot}05$. With this value we were able to calculate from the measurements of LaMer and Read a value for the heat of hydrolysis of Cr_2O_7'' (−1186 cals./mol.) that agrees very well with the heat effect of our kinetic measurements (−1210 cals./mol.). Moreover, a value for the heat of dissociation of the hydrochromate ion was obtained (−7860 cals./mol.) that agrees fairly well with the dependence on temperature of the dissociation constant (−6772 cals./mol.).

We consider these facts as proof that in the photochemical oxidation with dichromate, the ion Cr_2O_7'' represents the photoactive component. Its hydrolytic equilibrium precedes the photochemical reaction. With the increase of temperature the equilibrium shifts in favour of the hydrochromate ion. This corresponds to a decrease of the concentration of the photoactive component and consequently to a diminished reaction velocity.

An excitation of the electron is possible in such a complex ion if the light energy is absorbed by an electron shift into the empty orbit of the ion. Whether such a light absorption would lead directly to a photochemical reaction is, however, questionable (Bonhoeffer and Harteck, "Grundlagen der Photochemie," Dresden, 1933, p. 165). We suppose, therefore, that the primary photochemical reaction consists in a shift of an electron within the hydrated dichromate ion. By taking up energy, the ion becomes so unstable that it disintegrates into OH′, $HCrO_4'$, and CrO_3. For the photochemical oxidation of glycerol we must therefore suppose the following reaction mechanism :

$$Cr_2O_7'',HOH \rightleftarrows 2HCrO_4' - 1186 \text{ cals.}$$

(1) $Cr_2O_7'',HOH + \boldsymbol{Nh\nu} \longrightarrow OH' + HCrO_4' + CrO_3$ . . . . (k_1)

(2) $CrO_3 + HCrO_4' + OH' \longrightarrow Cr_2O_7'' + H_2O$ . . . . (k_2)

(3) $CrO_3 + C_3H_5(OH)_3 \longrightarrow CrO_2 + C_2H_3(OH)_2{\cdot}CHO + H_2O$ . . . . (k_3)

(4) $CrO_2 + CrO_2 \longrightarrow Cr_2O_4$

(5) $Cr_2O_4 + C_3H_5(OH)_3 \longrightarrow C_2H_3(OH)_2{\cdot}CHO + Cr_2O_3 + H_2O$

This accounts in the first place for the fact that the photochemical oxidation with dichromate is followed by production of an alkaline reaction. The formation of glyceraldehyde has been established by Bowen and his collaborators (Bowen and Bunn, *J.*, **1927**, 2353; Bowen and Yarnold, *J.*, **1929**, 1648), and Eder (*J. pr. Chem.*, 1879, **14**, 294) found CrO_2 and Cr_2O_4 in chromate–gelatin that had been exposed to light.

In this reaction mechanism CrO_3, CrO_2, and Cr_2O_4 have to be considered as unstable intermediates. If one assumes their concentration during the stationary period to be constant, the photochemical reaction velocity, after the usual calculations are done, can be expressed as follows :

$$+\frac{d[Cr_2O_3]}{dt} = \frac{k_1 I_{abs.}[C_3H_5(OH)_3]}{k_2[HCrO_4'][OH']/k_3 + [C_3H_5(OH)_3]}$$

In this and in the following equations the value $I_{abs.}$ is given by

$$I_{abs.} = I_0(1 - e^{-ip}[Cr_2O_7'',HOH])$$

This expression has been confirmed in every respect by experiment. From it follows, first, the linear dependence of the reaction velocity on the intensity of light (I_0), and secondly, the exponential deceleration of the reaction and the increase of the concentration of the $HCrO_4$ ion on the addition of alkali. From the above expression a non-linear increase of the reaction velocity with the increase of the concentration of glycerol must be expected. If the concentration of glycerol is low, however, the following expression showing a linear connection is valid :

$$+\frac{d[Cr_2O_3]}{dt} \approx \frac{k_1 I_{abs.}[C_3H_5(OH)_3]}{k_2[HCrO_4'][OH']/k_3}$$

If the concentration of glycerol is high, the reaction velocity according to the expression $+d[Cr_2O_3]/dt \approx k_1 I_{abs.}$ becomes independent of this concentration.

All these deductions from the expression have been fully confirmed by experiment. It can be inferred therefrom that the reaction mechanism, as described above, corresponds in principle to the actual reaction.

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