Further Studies on Kinetics of Reaction of Malachite Green with Acids. Influence of Temperature

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Lapin and Gein(1) suggested the use of malachite green (MG) as an analytical reagent especially for the colorimetric estimation of Sb^{3+}, Au^{3+} and Tl^{+}. For these estimation the interaction between metal ions and malachite green has been found sensitive to acidity. In acid medium, however, malachite green reacts with acid(2-4), resulting in the loss of characteristic color which sets a limitation to its usefulness in acid medium. This instability of malachite green in acid medium was hitherto uninvestigated in detail and therefore, warranted investigations for the elucidation of the mechanism involved therein. The variation of velocity constant with temperature could be utilized for the computation of energy, heat and entropy of activation, which are of immense value for the elucidation of reaction mechanism. In the present paper are reported the investigations on the reaction of MG with hydrochloric acid at different temperatures in aqueous medium as well as in media containing varying percentages of organic solvents.

Experimental

Malachite green of B. D. H. quality was purified in the manner described by Lewis and coworkers(5). The purified product used for kinetic study was obtained as sulfate. The hydrochloric acid used was Merck GR sample.

Acetone of B. D. H. Analar Grade was purified by refluxing over calcium oxide and distilling(6).

Dioxane, the extra pure product of E. Merck was purified by refluxing with acid and then over sodium and finally distilling according to procedure of Hess and Frahm(7).

The organic solvent water mixtures containing varying amounts of dioxane and acetone were made by volume percent. The reaction mixtures were so prepared that the final volume was the same containing fixed quantities of MG and acid but varying amounts of dioxane or acetone.

The progress of the reaction of MG with hydrochloric acid was investigated with the help of Beckman DU spectrophotometer by making optical density measurements at the wavelength of maximum absorption at different intervals of time. Corex cells of 10 mm. width were employed. The temperature in the cell compartment was maintained at the desired value by circulating water in the dual thermospacer set fixed in the spectrophotometer, from an external thermostat controlled by an electronic micro relay. By this arrangement temperature could be controlled with a precision of $\pm 0.05°C$.

Results and Discussion

Malachite green is known(4,5) to exhibit absorption maximum at $\lambda = 617.5\,m\mu$ in aqueous medium. This absorption maximum is, however, affected by the presence of organic solvents such as dioxane or acetone which shift it to 620.0 and 622.5 $m\mu$ respectively. The kinetic studies at different temperatures were therefore carried out at $\lambda = 617.5\,m\mu$ in water, 620 $m\mu$ in acetone and at 622.5 $m\mu$ in dioxane water mixtures. At these wavelengths MG obeys Beer's law and the reaction products do not show any absorption.

Time Variant Nature of the Reaction: First Order Nature.—In presence of acids the characteristic green color of MG decreases continuously and progressively with time. The data given in Fig. 1 illustrate the variation with time of optical density in presence of 60 mM hydrochloric acid. Here curves 1 to 6 refer to different initial concentration of MG employed, in the range 0.006~0.014 mM. Thus the concentration of hydrochloric acid is in very great excess over that of MG. Under this experimental condition the reaction obeyed first order law, when analyzed by differential method. The average value of n, the order of reaction corresponded to 1.11. The first order nature of the reaction is further substantiated by what follows.

For establishing the order of a reaction and to calculate velocity constant k from the values

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1) L. N. Lapin and V. O. Gein, *Trudy Komisii Anal. Khim., Akad. Nauk, S. S. S. R. Inst. Geokhim. i Anal. Khim.*, **7**, 217 (1956).

2) S. S. Katiyar, *Naturwissenschaften*, **49**, 325 (1962).

3) S. S. Katiyar, *Z. physik. Chem. N. F.*, in press.

4) N. V. Sidgwick and T. S. Moore, *J. Chem. Soc.*, **95**, 889 (1909), cf. *Chem. Abstr.*, **3**, 2799 (1909).

5) G. N. Lewis, T. T. Magel and D. Lipkin, *J. Am. Chem. Soc.*, **64**, 1774 (1942).

6) A. I. Vogel, "Practical Organic Chemistry", Longmans Green and Co., Ltd., London (1959), p. 171.

7) L. F. Fieser, "Experiments in Organic Chemistry", 2nd Ed., D. C. Heath and Co., New York, N. Y. (1941), p. 368.

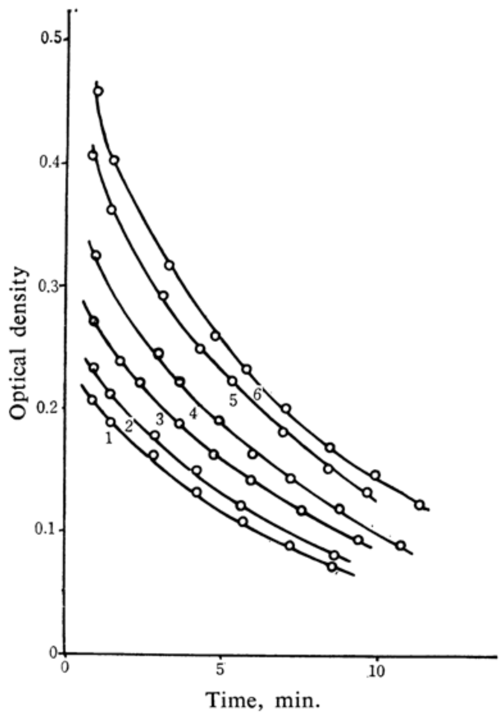

Fig. 1. Kinetic runs for the reaction of MG and HCl at varying MG concentrations.

1, 0.006	2, 0.007	3, 0.008
4, 0.01	5, 0.12	6, 0.14 mM

of C at time t, a number of methods[8] have been proposed from time to time. The following is the familiar equation for obtaining the first order rate constants

$$\ln C = \ln C_0 - kt$$

where C_0 is the initial concentration and C the concentration at time t. According to this equation the plot of $\log C$ vs. t would yield a straight line for a first order reaction. It is of interest to note from Fig. 2 that the plots of $\log C$ vs. t are sensibly linear confirming thereby the first order nature of the reaction. As mentioned above that $C_{\mathrm{MG}} \ll C_{\mathrm{H}^+}$ therefore the real velocity constant k' was obtained as follows:

$$k' = \frac{(\Delta \log C_{\mathrm{MG}})}{\Delta t\ (C_{\mathrm{H}^+})}\ \mathrm{l.\,mol^{-1}\,sec^{-1}} \qquad (2)$$

Dependence of k' on Temperature in Aqueous Medium.—The data given in Fig. 2 show the variation of log (OD) with time of malachite green solutions at different temperatures in the range 298∼313°K. For these experiments the initial concentrations of MG and hydrochloric acid were 0.008 and 40 mM respectively. From the slope of these plots and the known initial concentration of hydrochloric acid k' was computed and the values obtained are reported in Table I; k' were 3.56×10^{-2} and 6.77×10^{-2} $\mathrm{l.\,mol^{-1}\,sec^{-1}}$ at 298 and 308°K respectively. The data of Table I were analyzed by the Arrhenius equation

$$\ln k' = \ln A - \frac{RT}{E^{\neq}} \qquad (3)$$

and the results are given in Fig. 3. It is interesting to note that sensibly linear plot of $\log k'$ vs. $1/T$ was obtained in accord with the

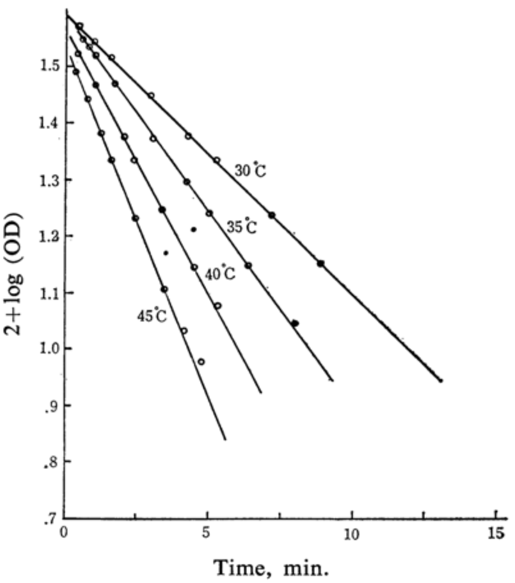

Fig. 2. Variation of log (OD) with time at different temperatures in aqueous medium.

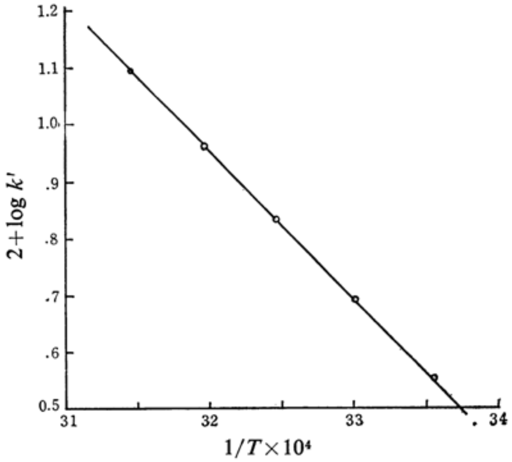

Fig. 3. Linear variation of $\log k'$ with $1/T$ in aqueous medium.

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[8] See for example, E. A. Guggenheim, *Philos. Mag.*, **2**, 538 (1926); A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", John Wiley & Sons, Inc., New York (1953), p. 40.

TABLE I. VELOCITY CONSTANT FOR THE REACTION OF MG AND HCl AT DIFFERENT TEMPERATURES IN AQUEOUS MEDIUM

Temp. °K	$k' \times 10^2$ l./mol. sec.
298	3.56
303	4.91
308	6.77
313	9.12
318	12.40

TABLE II. THERMODYNAMIC QUANTITIES OF ACTIVATION IN AQUEOUS MEDIUM AT 25°C

$E^{\neq}$	11.91	kcal.
A	1.92×10^7	l./mol.sec.
$\Delta F^{\neq}$	19.42	kcal./deg.mol.
$\Delta S^{\neq}$	-27.20	cal./deg.mol.
$\Delta H^{\neq}$	11.32	kcal.

above equation. The slope of this plot yielded a value of 11.91 kcal. for $E^{\neq}$, the energy of activation. This value of $E^{\neq}$ together with k' (given in Table I) gave a value of 1.92×10^7 l. mol^{-1} sec^{-1} for A, the frequency factor. Further, these data were also utilized for the computation of other thermodynamic quantities of activation such as free energy ($\Delta F^{\neq}$), entropy ($\Delta S^{\neq}$) and heat ($\Delta H^{\neq}$) of activation with the aid of following equations[9]

$$\Delta F^{\neq} = 2.303\, \boldsymbol{RT}\left(\log \frac{\boldsymbol{RT}}{Nh} - \log k'\right) \qquad (4)$$

$$\Delta S^{\neq} = 2.303\, \boldsymbol{R}\left(\log A - \log \mathrm{e}\frac{\boldsymbol{RT}}{Nh}\right) \qquad (5)$$

The values of themodynamic quantities are summarized in Table II. It is seen from this table that $\Delta S^{\neq}$ corresponded to -27.2 cal./deg. mol. This negative value of $\Delta S^{\neq}$ indicates that the reaction is occurring between ionic species[10,11].

Dependence of Velocity Constant on Temperature in Dioxane and Acetone - Water Medium.— A typical set of kinetic data obtained in 10% dioxane - water and 10% acetone-water is shown in Figs. 4 and 5 respectively. Similar type of data were obtained in 5 and 15% composition of these solvents. For these experiments the initial concentration of MG and hydrochloric acid were 0.008 and 80 mM respectively. The values of rate constants k' obtained from these data are listed in Table III. It may be noted from this table that k' decreased with the increase in percentage of organic solvent at a particular temperature. This lowering of k' with decrease of dielectric constant of the medium when examined from Bronsted, Christiansen and Scatchard[12] equation points out towards the like charged nature of reactants involved in the reaction. This aspect has already been discussed in detail in a separate communication[2,3]. Further, at a fixed composition of solvent, however, rate constant

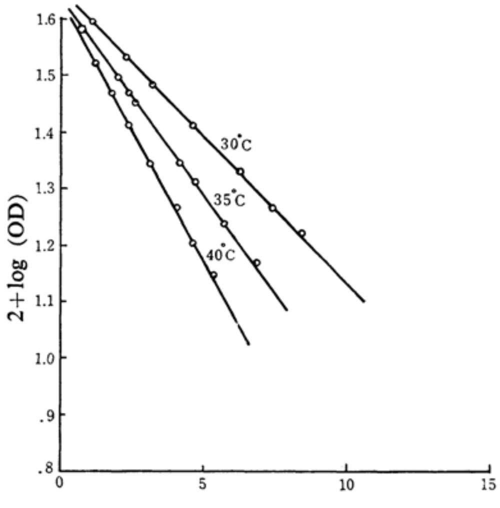

Fig. 4. Typical kinetic data for the reaction of MG and HCl in 10% dioxane.

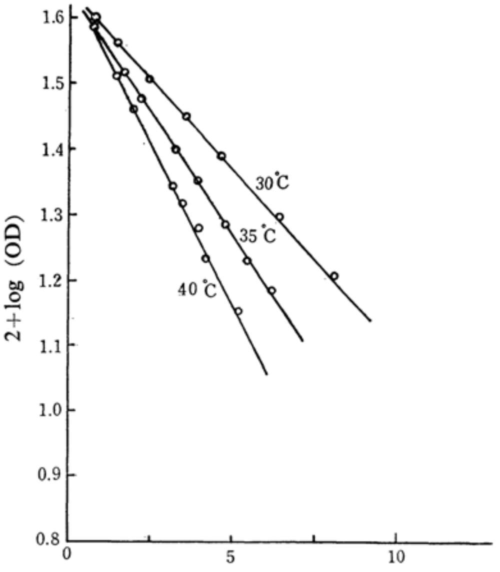

Fig. 5. Typical kinetic data for the reaction of MG and HCl in 10% acetone.

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[9] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", McGraw Hill Book Co., Inc., New York, N. Y. (1941), pp. 195—199.

[10] D. P. Ames and J. E. Willard, *J. Am. Chem. Soc.*, **73**, 164 (1951).

[11] Cf. Ref. 9., p. 433.

[12] G. Scatchard, *Chem. Revs.*, **10**, 229 (1932).

TABIE III. VELOCITY CONSTANTS FOR THE REACTION OF MG AND HCl AT VARYING TEMPERATURES IN ORGANIC SOLVENT WATER MIXTURES

Temp. °K	$k' \times 10^2$ l./mol.sec.		
	5%	10%	15%
	Dioxane		
298	2.32	1.85	1.44
303	3.27	2.48	1.90
308	4.47	3.33	2.58
313	6.00	4.42	3.43
	Acetone		
298	2.28	1.85	1.44
303	3.31	2.64	2.04
308	4.67	3.60	2.71
313	6.61	4.71	3.65

TABLE IV. THERMODYNAMIC QUANTITIES OF ACTIVATION IN ORGANIC SOLVENT WATER MIXTURES

Thermodynamic quantities		Percentage of organic solvent		
		5%	10%	15%
		Dioxane		
$E^{\neq}$,	kcal.	11.68	11.27	10.68
A,	l./mol.sec.	0.84×10^7	0.34×10^7	0.78×10^6
$\Delta F^{\neq}$,	kcal./deg.mol.	19.68	19.82	19.95
$\Delta S^{\neq}$,	cal./deg.mol.	−28.84	−30.67	−33.13
$\Delta H^{\neq}$,	kcal.	11.09	10.68	10.09
		Acetone		
$E^{\neq}$,	kcal.	12.75	11.70	11.16
A,	l./mol.sec.	3.11×10^7	0.70×10^7	0.22×10^7
$\Delta F^{\neq}$,	kcal./deg.mol.	19.68	19.81	19.95
$\Delta S^{\neq}$,	cal./deg.mol.	−26.24	−29.20	−31.52
$\Delta H^{\neq}$,	kcal.	12.16	11.11	10.57

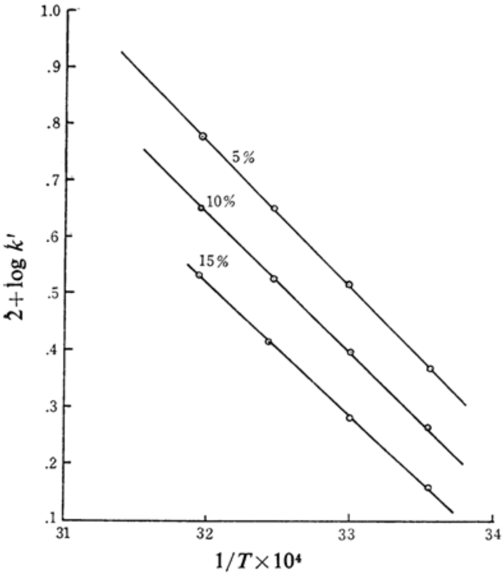

Fig. 6. Variation of log k' with $1/T$ in dioxane-water.

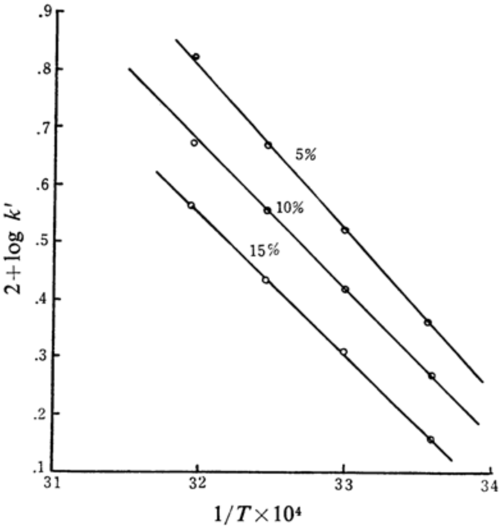

Fig. 7. Variation of log k' witth $1/T$ in acetone-water.

k' was found to increase with increasing temperature. Thus, e. g. in 5% dioxane k' was 2.32×10^{-2} and 4.47×10^{-2} l. mol^{-1} sec^{-1} at temperatures 298 and 308°K respectively. This gave a value of 1.92 for temperature coefficient which is of the same order as observed in case of a numder of other reactions[13].

The data of Table III were also employed for the calculation of $E^{\neq}$ in different composition of organic solvent. The plots of log k' vs. $1/T$ are shown in Figs. 6 and 7, for dioxane and acetone water mixtures. These plots as required by Eq. 3 are straight lines and the values of $E^{\neq}$ obtained from the slopes are returned in Table IV. It is instructive to note that $E^{\neq}$ decreases slightly with increasing percentage of organic solvent. Further the data of Table IV were also employed for the computation of thermodynamic quantities of activation such as $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta F^{\neq}$. The values of these in different solvent compositions are summarized in Table IV. It is instructive to observe that $\Delta S^{\neq}$ becomes more negative with increasing percentage of organic solvents. This is probably due to solvated nature of intermediate complex. This observation also suggests that the species involved in the reaction responsible for the fading of color of MG in acid media are similarly charged[14] and this is in accord with the earlier findings.

Reaction Mechanism.—The results obtained by the kinetic studies on the reaction of malachite green and hydrogen ions led the author to suggest the following mechanism

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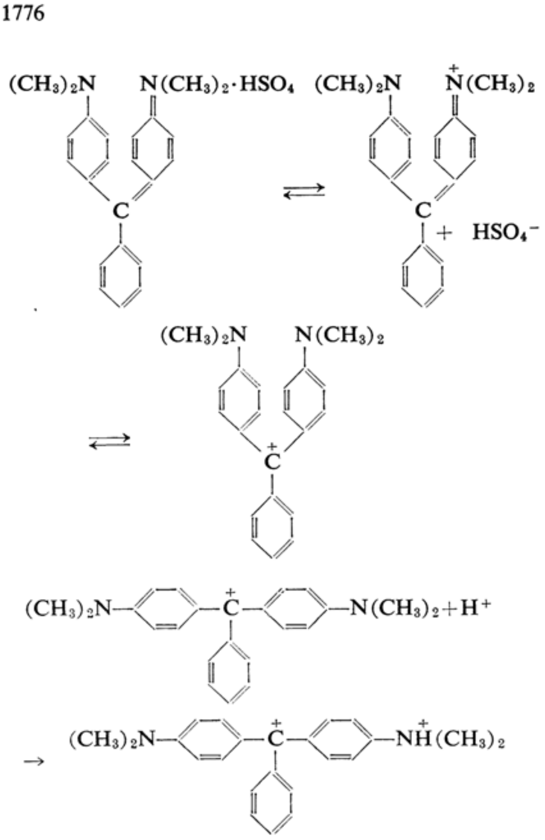
[13] S. Glasstone, "A Text Book of Physical Chemistry", MacMillan and Co., Ltd., London (1956), p. 1087.

[14] Cf. Ref. 9, p. 122.



It is suggested that the first step represented by an equilibrium between the HSO_4^- and MG^+ ion does not contribute to the kinetic studies as the ionic recombination processes are known to be very fast[15,16]. Therefore, the second step involving the formation of acid salt is the rate determining step. It is instructive to note here that the second step points out towards reaction between positively charged ions, which is in complete agreement with the kinetic data obtained and presented in this paper and other communications[2,3]. It will be of interest to refer in this connection the observation of Branch and Tolbert[17] and Newman and Deno[18] who have also suggested the formation of acid salt for the reaction of malachite green with acids at pH 1.

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[15] M-Eigen, *Discussions Faraday Soc.*, **17**, 194 (1954).

[16] P. Delahay and T. J. Adams, *J. Am. Chem. Soc.*, **74**, 1437 (1952).

[17] G. E. K. Branch and B. M. Tolbert, ibid., **71**, 781 (1949).

[18] M. S. Newman and N. C. Deno, ibid., **73**, 3644 (1951).