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EFFECT OF HEATING RATE ON ACTIVATION ENERGIES DERIVED BY A DYNAMIC KINETIC METHOD

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Alkaline fading of bromophenol blue was chosen for the investigation of the effect of heating rate on the activation energies derived from the dynamic kinetic method. Freeman and Carroll's treatment was adopted to compute the activation energies from experimental data taken with three heating rates: namely 1°, 0.5° and 0.25°/min. It was found that the activation energy increases as the heating rate decreases. This is attributed to the non-equilibrium conditions. By extrapolating to zero heating rate, the activation energy obtained is comparable to that obtained via classical isothermal kinetics.

In a previous paper [1] four dynamic kinetic equations (those of Freeman and Carroll, Coats and Redfern, Achar et al. and Horowitz and Metzger) were tested, using experimental data for the non-isothermal catalytic decomposition of H_2O_2 in aqueous solution. It was concluded that Freeman and Carroll's treatment gives the best result. It is well understood that for reactions in the solid phase the activation energy derived by a dynamic kinetic method is affected by many factors, such as the size of the sample, particle size, packing of the sample, pressure, the atmosphere under which the reaction takes place and the rate of heating. For reactions in solution, however, all these factors are eliminated, except for the last one. It is desirable therefore, to investigate the effect of heating rate on the energy of activation derived from the dynamic kinetic method. The alkaline fading of bromophenol blue in aqueous solution was chosen for this study. The experimental data were treated by Freeman and Carroll's method.

Experimental

0.6690 g of bromophenol blue (E. Merck, reagent grade) was dissolved in a small amount of absolute ethanol and treated with an equivalent amount of 0.1 *N* NaOH to convert it to the sodium salt. The solution was evaporated to dryness on a water bath and then dissolved in water and made up to 1000 ml. The concentration of the bromophenol blue solution thus prepared was 10^{-3} *M*. 50 ml was pipetted into a 120 ml Erlenmeyer flask, which was set in a water bath together with standard 1 *N* NaOH solution kept in a plastic bottle. The water bath was then cooled down to low temperature with ice. When the two solutions had reached thermal equilibrium with the water bath, the water bath was heated up linearly by manual control of a rheostat, at a pre-determined rate. Three heating rates were employed: 0.25°, 0.5°, and 1° per minute. The time and temperature were then recorded. 20 ml of the standard 1 *N* NaOH solution was pipetted into the Erlenmayer flask containing the bromophenol blue solution. The reaction flask was shaken to ensure thorough mixing and good thermal exchange with the water bath. 5 ml of sample was taken at suitable time intervals and delivered into a 50 ml volumetric flask containing an equivalent amount of HCl to neutralize the alkali in the sample. After dilution with distilled water the absorbance was measured at 595 mμ with a Unicam spectrophotometer, using a blue light source.

Results and discussion

Under the experimental conditions employed, the alkaline fading of bromophenol blue, is a pseudo first-order reaction, i.e. it behaves as a first-order reaction kinetically. The activation energy of this reaction has been determined by Amis and La Mer [2] and Chen and Laidler [3]. The absorption of light by bromophenol blue obeys Beer's law.

The results of a dynamic run at a heating rate of 1° per minute are shown in Fig. 1, in which the optical density of the diluted sample, taken as $(a - x)$, is plotted against time; where a represents the initial concentration and x the amount reacted at time t. The rate, $\frac{dx}{dt}$, is taken as the negative slope of the tangent drawn

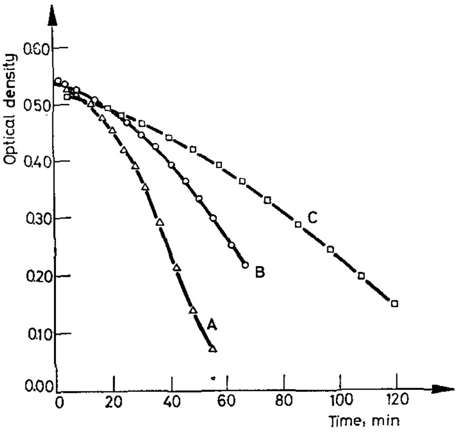

Fig. 1. Reaction course for the alkaline fading of bromophenol blue. △ 1°/min, ○ 0.5°/min, □ 0.25°/min

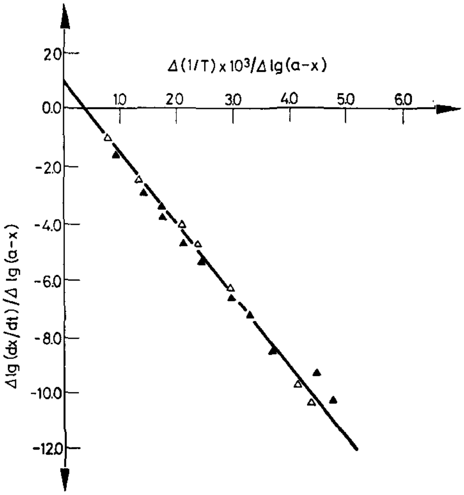

Fig. 2. Freeman and Carroll's plot for the alkaline fading of bromophenol blue at a heating rate of 1°C/min

at the desired point. The treatment of the data by Freeman and Carroll's method is shown in Table 1 and two separate runs are plotted in Fig. 2. A straight line could be drawn through all the points and also the theoretical intercept of unity on the ordinate. From the slope of the line, an activation energy of 11.4 kcal/mole was obtained.

The results of a dynamic run at a heating rate of 0.5° per minute are shown in Fig. 1. The treatment of the data by Freeman and Carroll's method is shown in Table 2, and are plotted in Fig. 3 similar to the Fig. 2. An activation energy of 12.2 kcal/mole was calculated from the slope of the straight line.

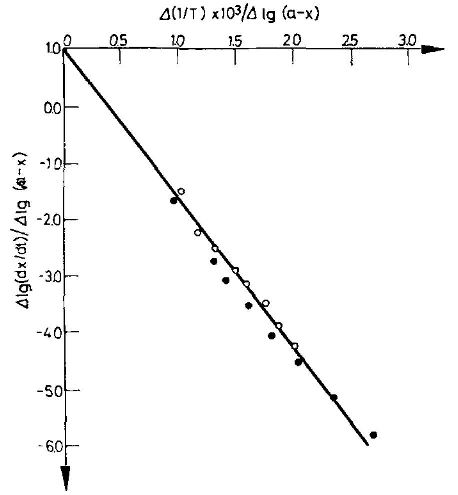

Fig. 3. Freeman and Carroll's plot for the alkaline fading of bromophenol blue at a heating rate of 0.5°C/min

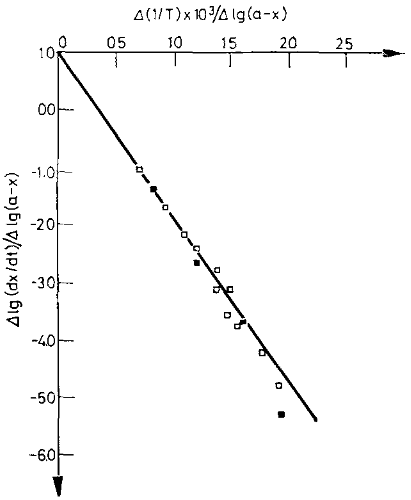

Fig. 4. Freeman and Carroll's plot for the alkaline fading of bromophenol blue at a heating rate of 0.25°C/min

The results of a run at a heating rate of 0.25° per minute are shown in Fig. 1. Freeman and Carroll's treatment is shown in Table 3 and two runs are plotted in Fig. 4. From the slope of the line, an activation energy of 13.4 kcal/mole was obtained.

The above results indicate that the activation energy of a chemical reaction obtained by the dynamic kinetic method increases as the heating rate decreases. This is inconsistent with the result found by Dharwadkar and Karkhanavala in their thermogravimetric analysis of calcium oxalate [4]. The reason can be explained as follows. Equilibrium is not reached in the dynamic method, whereas it is in the isothermal method. Suppose, in the isothermal method, that a ten degree increase in temperature will double the rate of a certain chemical reaction. If the dynamic method is used to investigate this reaction, although the temperature of the water bath has increased by ten degrees, the increase in temperature of the sample may be less than ten degrees. Consequently, the rate of the reaction will also be less than doubled; this results in a low activation energy. The faster the heating rate, the larger will be the deviation from equilibrium, and the lower the derived activation energy. This effect is pronounced in solid-phase reactions, especially when the size of the sample is large. If the derived activation energies are plotted against the heating rates, and the straight line extrapolated to zero heating rate, the value obtained should represent the true activation energy. In the present case, the value thus found is 14.0 kcal/mole, which is comparable to the accepted value of 12.2 kcal/mole [3].

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Résumé — On a choisi la décoloration du bleu de bromophénol en milieu alcalin pour étudier l'influence de la vitesse de chauffage sur l'énergie d'activation calculée à partir des données fournies par une méthode d'étude cinétique dynamique. On a adopté la méthode de Freeman et Carroll pour calculer les énergies d'activation à partir des données expérimentales obtenues avec trois vitesses de chauffage, à savoir 1°, 0.5° et 0.25°/min. On montre que l'énergie d'activation augmente quand la vitesse de chauffage diminue. On attribue ce phénomène aux conditions de non-équilibre. En extrapolant pour une vitesse de chauffage nulle, on obtient une énergie d'activation comparable à celle calculée par la méthode classique en cinétique isotherme.

Zusammenfassung — Die in alkalischem Medium erfolgende Entfärbung von Bromphenolblau wurde zum Studium des Einflusses der Aufheizgeschwindigkeit auf die nach der dynamischen kinetischen Methode erhaltenen Aktivierungsenergien herangezogen. Das Verfahren von Freeman und Carroll wurde zur Berechnung der Aktivierungsenergien aus Versuchsdaten, welche bei drei Aufheizgeschwindigkeiten, nämlich 1°, 0.5° und 0.25°/min erhalten worden waren, verwendet. Es wurde festgestellt, daß die Aktivierungsenergie mit abnehmender Aufheizgeschwindigkeit zunimmt. Der Grund hierfür wird den Nicht-Gleichgewichtsbedingungen zugeschrieben. Wird auf Aufheizgeschwindigkeit = 0 extrapoliert, so ist die erhaltene Aktivierungsenergie mit der nach klassischer isothermer Kinetik erhaltenen vergleichbar.

Резюме — Обесцвечивание в щелочной среде бромфенола синего было выбнано для исследования влияния скорости нагрева на величинй энергии активации, рассчитанной по данным динамического метода. С целью расчета энергии активации по экспериментальными данным, полйченным при трех скоростях нагрева (1°, 0,5°, и 0,25°/мин) использован метод Фримена и Керрола. Установлено, что энергия активации увеличивается по мере уменьшения скорости нагрева.