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A Conductometric Study of The Influence of Concentration And Temperature On The Reaction Velocity of 2,4-Dinitrochlorobenzene With Piperidine in 95 Per Cent Ethanol

F. E. JACOB AND CHARLES O. FRANK

Abstract. The reaction kinetics of 2,4-dinitrochlorobenzene and piperidine in 95 per cent ethanol were determined by a Kohlrausch conductometric technique. A 1000 cps audio-frequency oscillator was used with both headphones and oscilloscope employed as null-point detectors. Three temperatures and concentrations were used with average specific rate constants of 0.3188, 1.744, and 4.423 liters mole⁻¹ minute⁻¹ at 0.2°C, 25°C, and 40°C respectively. The change in entropy was -21.84 cal. deg.⁻¹ mole⁻¹ and the activation energy was 10.58 Kcal.

Determination of reaction rates has been accomplished by various means which utilizes either chemical or physical properties of the reaction components. The use of a chemical property implies a direct concentration determination by standard quantitative methods. Important restrictions to these methods are the need to: 1.) make standard solutions, 2.) remove an aliquot of the reacting solution, 3.) quench the reactions, and 4.) derive conclusions on a few discontinuous readings.

The more convenient is the physical method. It is necessary for the physical property to change linearly with the changing concentrations of the reactants and products. Many chemical reactions which proceed with the formation or disappearance of ions, are feasible for conductometric studies. The reaction between 2,4-dinitrochlorobenzene and piperidine in 95 per cent ethanol proceeds with the formation of dinitrophenylpiperidine, chloride ions, and piperidinium ions.

All reaction kinetics of this reaction have been obtained by methods which necessitated the removal and quenching of aliquots of the reacting solution. It would be of interest to study this reaction by a method which would allow the progress of the reaction to be followed continuously and at the temperature at which the reaction was taking place.

The problem was to determine conductometrically the reaction velocity and Arrhenius parameters for the reaction at various concentrations and temperatures.

EXPERIMENTAL

Resistances (R_t) of the reacting solutions after known times

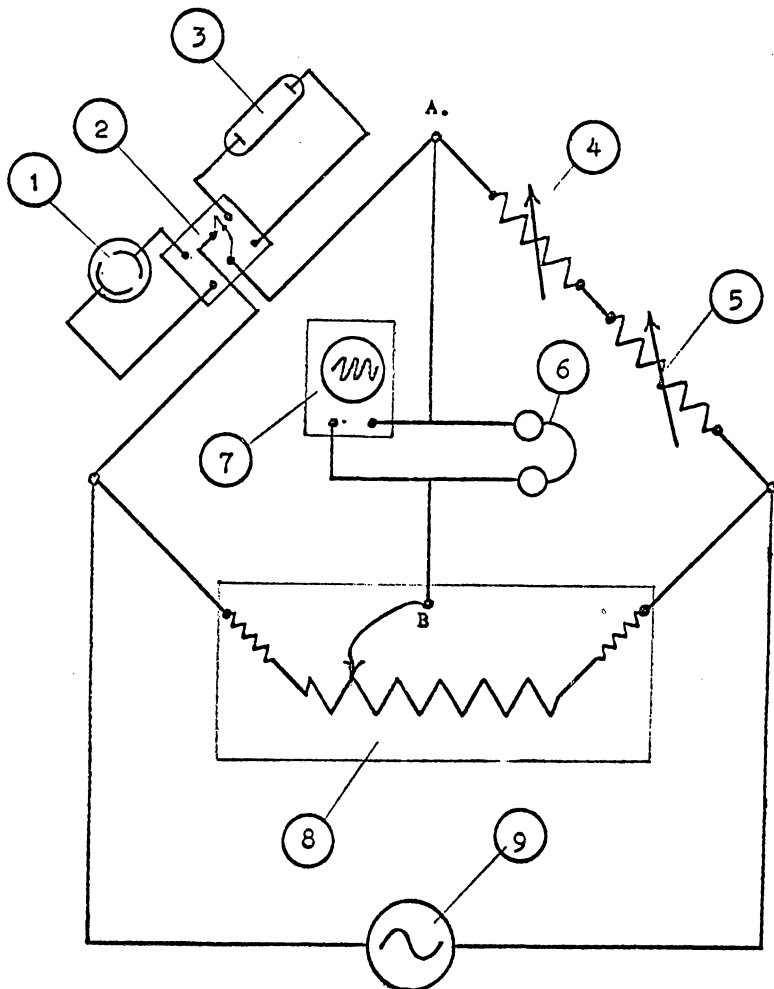


Figure 1. Schematic diagram of conductivity apparatus

1. Conductivity cell A
2. Double-pole, double-throw switch
3. Conductivity cell B
4. General Radio decade resistor, type 1432-P
5. General Radio decade resistor, type 1432-Q
6. Headphones
7. Oscilloscope
8. Leeds & Northrup slide wire
9. Signal generator

had elapsed from the start of the reactions were measured using the Wheatstone bridge method of Kohlrausch (Figure 1).

Coarse bridge balances were first made with two decade boxes which gave a range of one-tenth ohms to one megohm. A student Kohlrausch slidewire was used to obtain a more precise balance between the decade boxes and the conductivity cell. The conductivity cells A and B were of the Kohlrausch type

with cell constants of 0.1244 cm^{-1} and 1.4359 cm^{-1} respectively. The null points were determined using both an oscilloscope and headphones. It was found that the oscilloscope allowed a quicker, more definite null point detection for high resistances, while the headphones were more sensitive at the end of the reaction where the resistances were lower and not changing rapidly.

Concentrations of 2,4-dinitrochlorobenzene solutions in 95 per cent ethanol were prepared such that the number of moles of solute placed in the cell would be .001 moles, .002 moles, and .0025 moles. The concentrations of the piperidine solutions introduced into the cells to initiate the reactions were twice the concentrations of the corresponding 2,4-dinitrochlorobenzene solutions.

The procedures used in this experiment were as follows:

1. Introduce proper volume of 2,4-dinitrochlorobenzene solution by means of a 50 milliliter buret.
2. Immerse the cell in water bath controlled to the nearest 0.1 degree centigrade.
3. Introduce the piperidine solution (at the same temperature as in 2.) by means of a pipet (for 25°C) or by a hypodermic syringe (for 0.2°C and 40°C).
4. Measure the time for the first few null points to reach preset resistances.
5. Measure the resistances of the reacting solutions for specific known times after the reaction has started and until a constant resistance is obtained.

Bunnett and Crockford (1) and other experimenters found the reaction to be of second order in 95 per cent ethanol. This reaction proceeds in two steps with the first being the slow or rate determining step.

Since the initial concentration of piperidine was exactly twice the concentration of 2,4-dinitrochlorobenzene, the reaction rate expression is simplified to $dx/dt = 2k(a-x)^2$ where a is the original concentration of 2,4-dinitrochlorobenzene and x is amount of chloride ion produced at a time t .

The total conductance (C) of the solution can be shown to be

$$C = \frac{\sum c_y m_y}{1000K_{\text{cell}}}$$

where c = concentration of ionic species in equivalents per liter

m = equivalent ionic conductance

and K_{cell} = cell constant.

For the reaction being considered, three conductances are

$$C_0 = \frac{(2a_{\text{pip.}})}{1000K_{\text{cell}}}$$

$$C_t = \frac{x \text{ mCl}^- + x \text{ m piperidinium} + (2a - 2x) \text{ m piperidine}}{1000K_{\text{cell}}}$$

$$C_\infty = \frac{(a \text{ mCl}^- + a \text{ m piperidinium})}{1000K_{\text{cell}}}$$

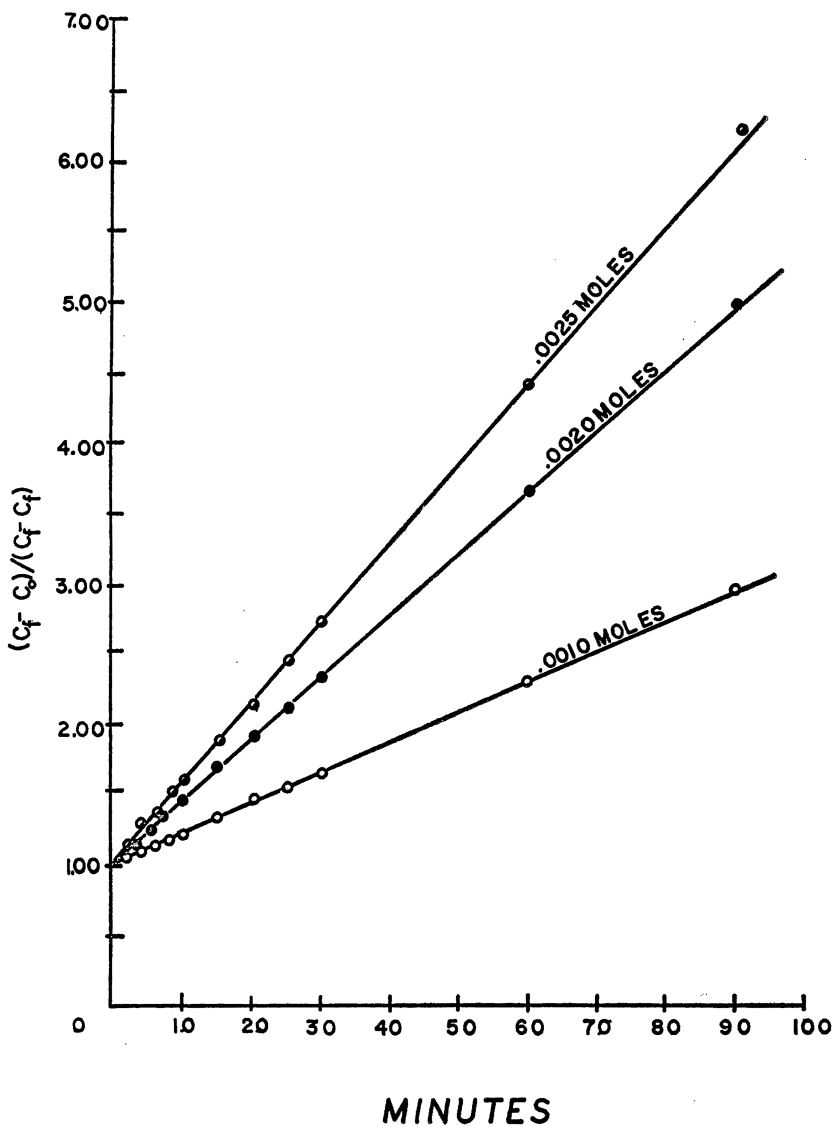


Figure 2. Increase in conductance ratio with time and at 0.2 centigrade

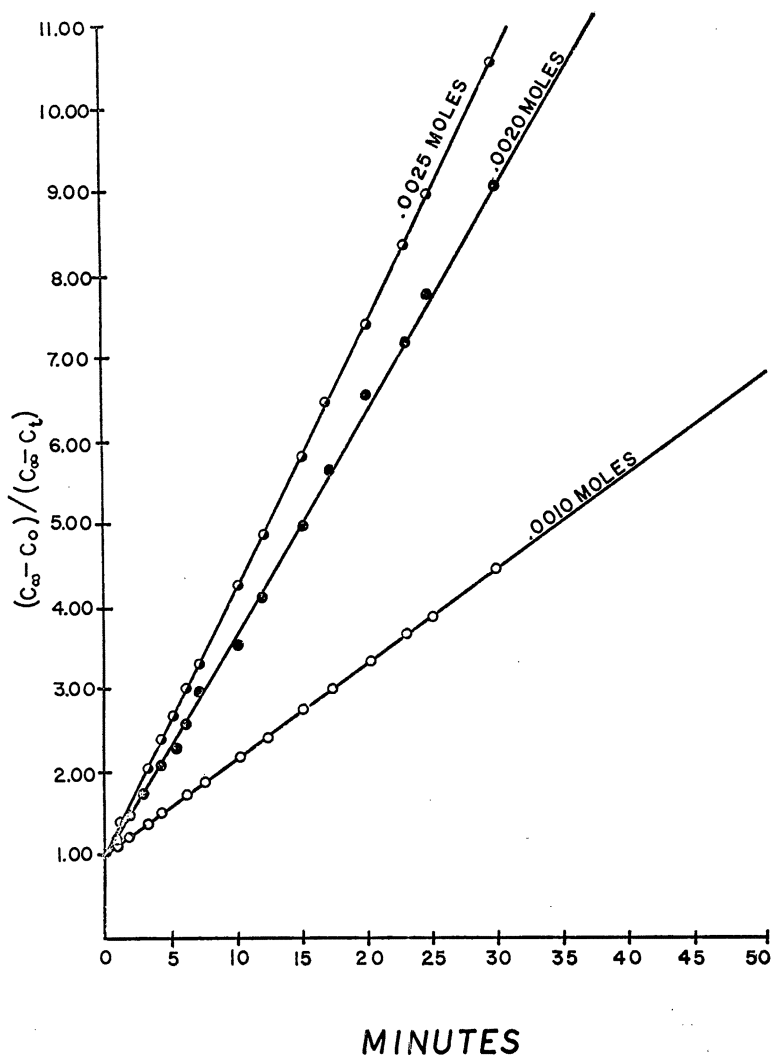


Figure 3. Increase in conductance ratio with time and at 25 centigrade

where C_0 , C_t , and C_∞ are conductances at times 0, t , and ∞ minutes respectively.

The change of conductance due to the reaction was simplified

$$\text{to } \frac{C_t - C_0}{C_\infty - C_0} = \frac{x}{a}$$

Solving for x in the above expression and substituting into the integrated rate equation ($-\frac{1}{a-x} = 2kt + 1/a$) permitted the rate

to be expressed in terms of conductances, which are linear functions of the molar concentrations. The substituted rate equation becomes

$$\frac{C_{\infty} - C_o}{C_{\infty} - C_t} = 2kat + 1$$

which is in the point slope form of a straight line. Each point plotted is the average of five determinations. The slopes and y- intercepts of the best lines through the plotted points were obtained by methods of least squares. The graphs obtained for two temperatures at the three concentrations are given in Figures 2 and 3.

Using Arrhenius's equation in the form

$$\log k = \log A - \frac{E}{2.303 RT}$$

and plotting $\log k$ versus $1/T$, the frequency factor (A) and the energy of activation(E) can be obtained (Figure 4).

The change in entropy was found using the following thermodynamic expression

$$\log k = \frac{S^*}{2.303 R} - \frac{E}{2.303 RT} + \log \frac{RT}{Nh}$$

where N is Avogadros number and h is Planck's constant.

DISCUSSION AND CONCLUSIONS

A conductometric method for determining the reaction kinetics of 2,4-dinitrochlorobenzene with piperidine in 95 percent ethanol was satisfactory. The absolute error was large at the beginning of the reaction because of the magnitudes of the resistances measured. The corresponding relative errors were generally less than 0.4 per cent for an individual measurement and 0.2 per cent for the deviation of the mean. The absolute error decreased with the progress of the reaction but the relative error remained constant.

When the conductance ratios for the three concentrations at one temperature were plotted against the time of the reaction, three straight lines were formed which radiated from a nearly constant y- intercept of 1. The fact that straight lines were obtained verified the equations relating the conductances with the specific rate constants. The close proximity of the points to the lines gave another indication of the precision of the method.

The specific rate constants are given in Table 1. As can be seen, the rate constants changed only with temperature. The average rate constant for both cells at 0.2°C, 25°C, and 40°C were 0.3188, 1.744, and 4.423 liters mole⁻¹ minute⁻¹ respectively. The values obtained by Bunnett and Crockford (2) by volumetric titrations of the chloride ions and by spectrophotometric

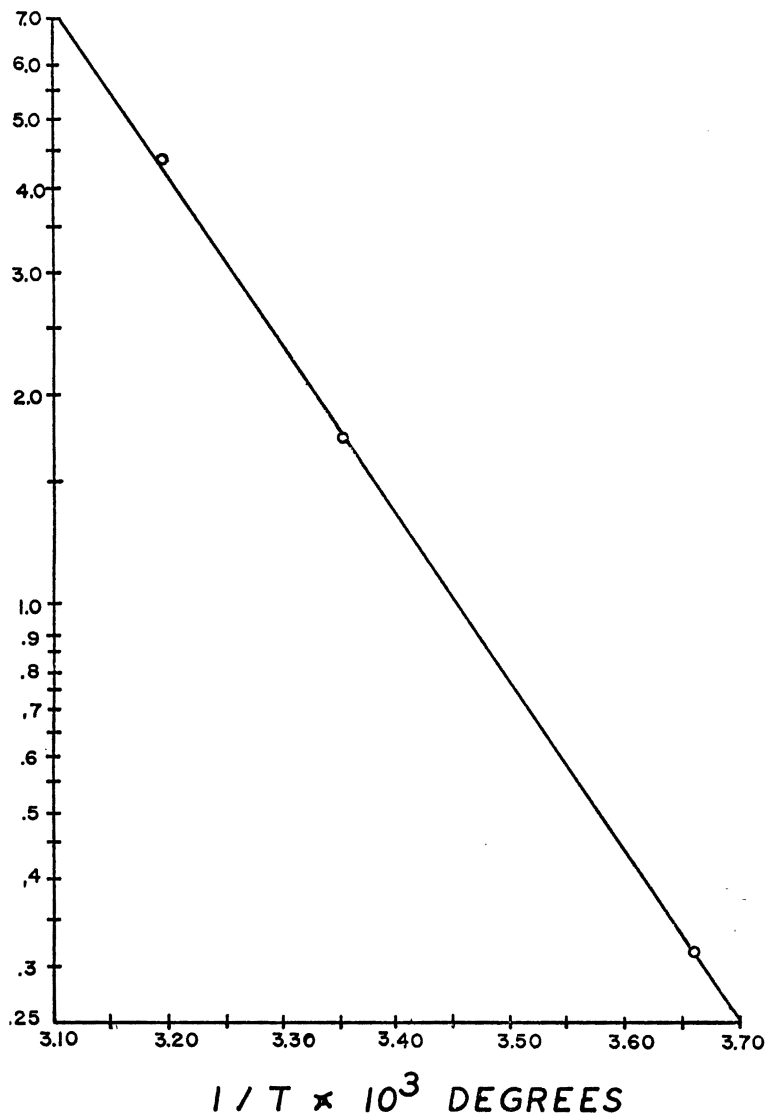


Figure 4. Variation of $\log k$ with the reciprocal of absolute temperature

analysis were smaller than by corresponding conductometric methods. It seems plausible that a continuous monitoring of the reaction progress would be the most accurate.

The slope in Figure 4 equalled -2.313×10^3 and the activation energy was 10.66 Kcal. The activation energy obtained from using the rate equation integrated between limits was 10:58 Kcal.

Table 1. Specific rate constant at various concentrations and temperature

Cell conc. in moles of 2,4-dinitrochloro- benzene	k (liter mole ⁻¹ minute ⁻¹)		
	0.2°C	25°C	40°C
.0010	0.3263	1.603	4.127
.0020	0.3212	1.834	4.526
.0025	0.3238	1.797	4.909
Cell B			
.0010	0.3229	1.650	4.195
.0020	0.3064	1.754	4.094
.0025	0.3122	1.825	4.732

The change in entropy of the system was -21.84 cal. deg.⁻¹ mole⁻¹.

Literature Cited

1. J. F. Bunnett and H. D. Crockford. *J. Chem. Ed.* 33, 556 (1956).
2. *Ibid.* p. 553.

Trace Analysis of Halogens by Neutron Activation

RALPH O. ALLEN JR.

Abstract. A procedure was developed by which trace quantities of chlorine, bromine, iodine, tellurium, and uranium could be quantitatively determined simultaneously in a single meteorite sample. Meteoritic material was irradiated with thermal neutrons. Carrier ions were added, the material was fused with sodium peroxide and the chlorine, bromine, and iodine were isolated. Distillation from a sulfuric acid solution removed the halogens from the bulk of material. After distillation, selective solvent extractions were used to separate and purify each of the halogens. The purified halides were precipitated as the silver halides, weighed, mounted, and counted by β , γ , and/or β - γ coincidence counting techniques.

INTRODUCTION

The problem of analysis of halogens in meteorites is characterized by the unique nature of the matrix and the trace concentrations of halogens present. The difficulty of conventional wet analysis of such samples has contributed to a lack of reliable data for halogen content of meteorites and rocks. Extreme care is necessary to avoid loss of volatile halides during

¹ The actual experimental work was done at Argonne National Laboratory while the author was participating in the ACM-Argonne Semester Program and the ANL Student Research Aide Program.