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A Conductometric Study of the Reaction Velocity of Halodinitrobenzene with Piperidine

F. EMMITT JACOB¹ AND TERRILL R. BERKLAND

Abstract. The rates of reaction for 1-chloro-, 1-bromo-, and 1-iodo-2,4-dinitrobenzene and piperidine in 95% ethanol were determined for various concentrations and temperatures by a conductometric process. An RC-18 Conductivity Bridge with an oscilloscope detector was found to be very satisfactory in the study. The specific rate constants gave the halogen reaction series $Cl > Br \gg I$ at all temperatures and concentrations used. The conductometric method for determining reaction velocities has shown itself to be very effective since it allows continuous monitoring of the system thereby eliminating the necessity of a chemical analysis.

Reaction velocity is the quantitative rate of change in the reactants per unit time. To measure reaction velocity, it is necessary to use either a chemical or physical process. In the chemical process, which is the more common, it is necessary to determine the concentration of one of the reactants or products at the moment the sample is removed from the main solution. There are complicated procedures to quench the solution by dilution, rapid cooling or addition of another reagent followed by back titration. All of these involve much time and are limited to reactions that proceed more slowly. In the physical process, the rate of reaction is determined by a change in physical property such as color to eye or instrument, refractive index, or electrical conductance.

In the conductance method, one can detect the disappearance or addition of ions in a solution provided there is no reaction between the reagents and the products which would produce a nonlinear function. The reaction between 1-halo-2,4-dinitrobenzene and piperidine has shown itself to be adaptable to the conductometric analysis.

The 1-chloro-2,4-dinitrobenzene reaction was performed only at 25° C. to compare the results of Frank (3) with the present work.

The rate of reaction between 1-chloro-2,4-dinitrobenzene had been carried out using a volumetric chemical analysis and a spectrophotometric analysis (1). Frank (3) showed that the conductometric analysis was superior to the chemical analysis and comparable to the spectrophotometric analysis which also allows continuous monitoring of the system. The purpose of this study was to apply the conductometric process to other areas of research and complete the reactivity series for 1-halo-2,4-dinitrobenzene with piperidine 95% ethanol.

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PROCEDURE

A Model RC-18 Conductivity Bridge which consisted of a Wheatstone Bridge, oscilloscope detector, and AC circuitry was employed. Two Kohlrausch cells, one designed for medium conductances and the other for low conductances were immersed in a constant temperature water bath. Temperatures used were 0.1° C. (ice mixture), 25.0° C., and 40.0° C. The cells were connected to the bridge during the reaction with shielded, insulated, copper wire. Platinum black was coated on the surface of the cell's platinum electrodes. For the concentrations of the reactants, a certain number of moles were used per cell volume. Cell 1 (medium conductance) had a volume of 40.0 ml. while Cell 2 (low conductance) was only 28.0 ml.

For the 1-chloro-2,4-dinitrobenzene reaction, six solutions, three for each cell, were prepared at 0.001, 0.002, and 0.0025 moles per cell volume. These were actually prepared in more concentrated form so that when 10 ml. solutions containing the corresponding number of moles of piperidine were added, the total solution would be brought to cell volume. This reaction was run only at 25° C. to check the results obtained by Frank (3).

Since the bromo and iodo homologs were not as soluble as the chloro, solutions were prepared for each cell so that cell volume would be reached upon addition of piperidine solution as described above. The final concentrations of the solutions for each cell were 0.0005, 0.00075, and 0.0010 moles per cell volume. In all cases, the moles of piperidine per cell volume were exactly double that of the corresponding halodinitrobenzene solution to simplify the mathematics used in the determination of the reaction rates.

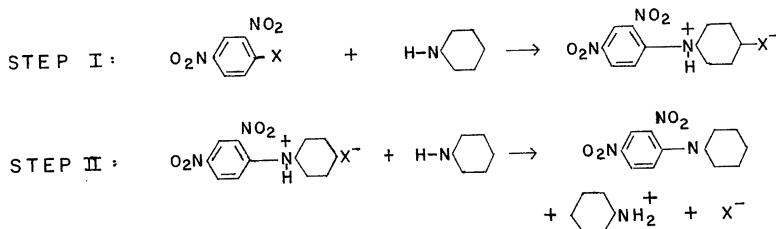
To start the reaction, a cell containing the prepared solution of halodinitrobenzene was injected with a syringe containing 10 ml. of the proper piperidine solution. Both reactants were kept at the desired temperature before injection. Each reaction was followed by measuring the conductance of the cell at specific time. This was done at least until the half-life of the reaction was reached which ranged from 12 hours for the iodo group (0.1° C.) to 10 minutes for the bromo group (40.0° C.). The conductances at infinite time were taken when the reaction had approached equilibrium which ranged from 1-7 days depending on the reactivity of halogen, temperature, and concentration.

CALCULATIONS

The velocity of a reaction can be expressed by the quantity dc/dt where dc is the change in concentration of one of the reac-

tants and dt is the change in time. This derivative is a function of the concentration of the reactants and can be equated provided a constant, k , known as the rate constant, is inserted into the relationship. The rate constant has the dimensions of $(\text{moles/liter})^{1-n} \text{sec}^{-1}$ where n is the order of the reaction.

Bunnett (1) found the reaction between 1-halo-2,4-dinitrobenzene and piperidine in 95% ethanol proceeds in two steps as follows:



where X is the halogen substituent. The rate for a second order reaction, provided there are two moles of piperidine for every mole of 1-halo-2,4-dinitrobenzene, can be expressed as: $dx/(a-x)^2 = 2kdt$ where dx is the change in concentration of either of the products, dt is the change in time, and a is the initial concentration of the 1-halo-2,4-dinitrobenzene. Upon integration, this becomes $1/(a-x) = 2kt + 1/a$ showing a linear equation which allows a plot of concentration $(a-x)$ versus time to have a slope of $2k$ (rate constant).

Since equivalent conductance is due to each of the ionic species, in the reaction studied, the three conductances that must be determined are:

$$C_o = (a_1 l_1) / 1000 K$$

$$C_t = [(2a-2x)_1 l_1 + x_2 l_2 + x_3 l_3 + x_4 l_4] / 1000 K$$

$$C_\infty = (x_2 l_2 + x_3 l_3 + x_4 l_4) / 1000 K$$

where l_n is the specific ionic conductance of ions 1,2,3, and 4, subscripts o,t , and ∞ are the conductances at times zero, t , and infinity, respectively, subscript 1 signifies the conductance of piperidine, subscript 2 signifies the conductance of product 2,4-dinitrophenylpiperidine, subscript 3 signifies the conductance of piperidinium ion, subscript 4 signifies the conductance of halide ion, and K is the cell constant.

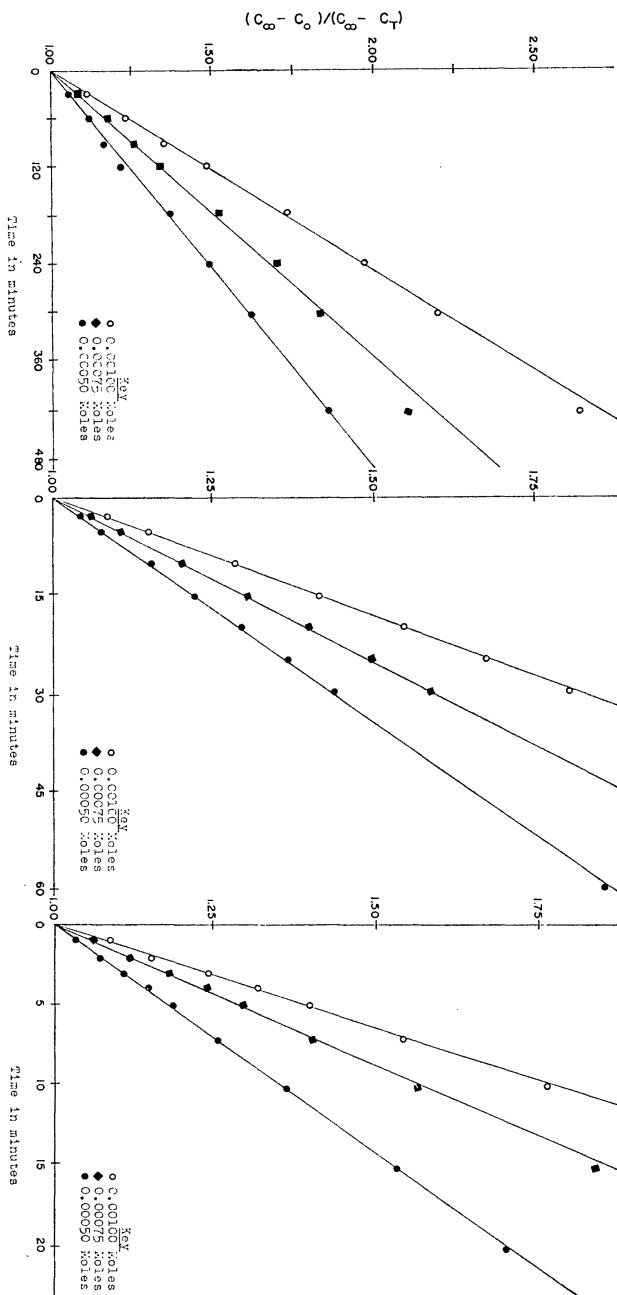


Figure 1. Increase in conductance ratio with time: 1-iodo-2,4-dinitrobenzene in cell 2 at 0.1° C., 25.0° C., and 40.0° C., respectively.

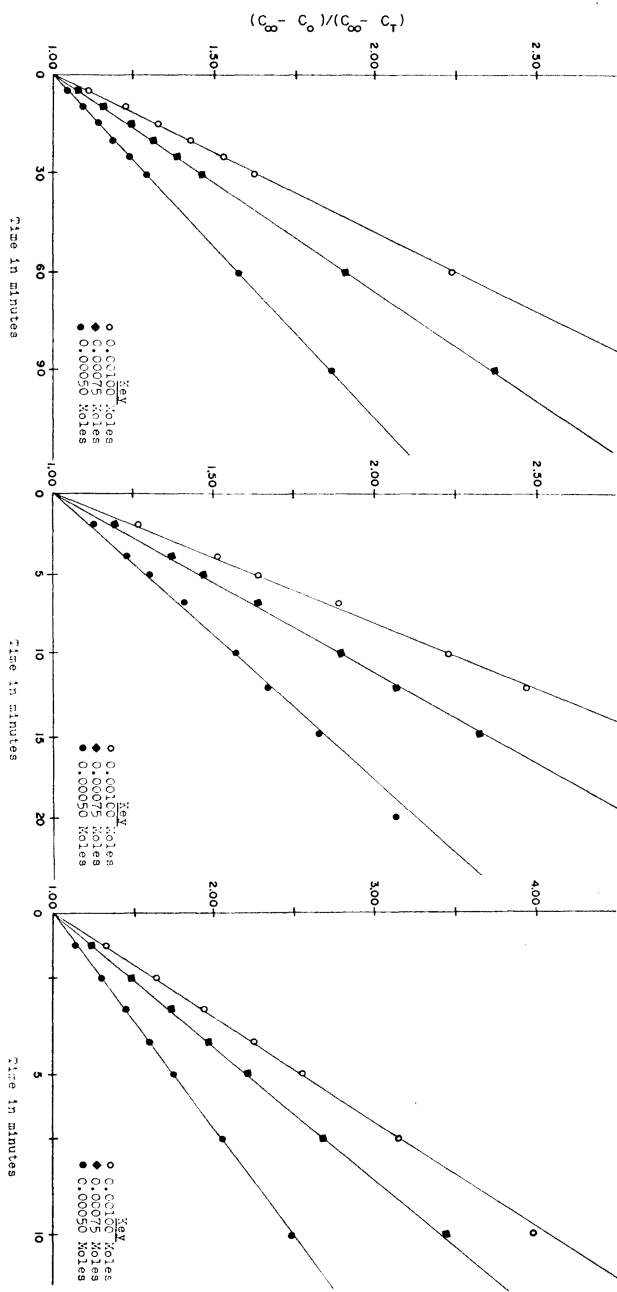


Figure 2. Increase in conductance ratio with time: 1-bromo-2,4-dinitrobenzene in cell 2 at 0.1° C., 25.0° C., and 40.0° C., respectively.

By subtracting C_0 from both C_t and C_∞ and by a division of the proper terms, an expression is obtained in which the cell constant and equivalent ionic conductances are eliminated leaving:

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

which, when substituted into the integrated rate equation above becomes:

$$\frac{C_\infty - C_0}{C_\infty - C_t} = 2kat + 1 = \text{conductance ratio.}$$

Therefore, a plot of conductance ratio against time will give a slope of $2ka$ and a y-intercept of 1. To determine the slope of the line, the method of least squares was used. Typical graphs obtained from the above method are shown in Figures 1 and 2. Figure 1 shows the slopes for the 1-iodo-2,4-dinitrobenzene reaction while Figure 2 shows slopes for the 1-bromo-2,4-dinitrobenzene reaction. From the slope of the lines, the rate constant, the half-life, the energy of activation, and change in entropy can be determined.

Table 1. SPECIFIC RATE CONSTANTS FOR THE 1-iodo- and 1-BROMO-2, 4-DINITROBENZENE REACTIONS WITH PIPERIDINE AT VARIOUS CONCENTRATIONS AND TEMPERATURES

Moles of halo-dinitrobenzene for 40 ml. cell volume	k (liter mole ⁻¹ minute ⁻¹)					
	iodo group			bromo group		
	0.1°C	25°C	40°C	0.1°C	25°C	40°C
0.00050	0.0583	0.3880	0.960	0.2616	1.385	3.946
0.00075	0.0560	0.3248	0.987	0.2729	1.566	4.196
0.00100	0.0554	0.3430	1.032	0.2762	1.623	4.280
Moles of halodinitrobenzene for 28 ml. cell volume	Cell 2					
0.00050	0.0563	0.3931	0.967	0.2654	1.358	4.161
0.00075	0.0541	0.3521	1.064	0.2811	1.715	4.611
0.00100	0.0550	0.3661	1.034	0.2916	1.769	4.099

Table 2. RATE CONSTANTS, ENERGY OF ACTIVATION, AND ENTROPY VALUES FOR THE 1-HALO-2,4-DINITROBENZENE REACTION WITH PIPERIDINE IN 95% ETHANOL

Halogen group	k (liter mole ⁻¹ minute ⁻¹)			E (Kcal.)	S* (calorie degree ⁻¹ mole ⁻¹)
	0.1°C	25°C	40°C		
Chloro ^a	0.3188	1.744	4.423	11.16	-19.97
Bromo-	0.2748	1.588	4.216	11.59	-18.74
Iodo-	0.0056	0.360	1.007	12.28	-19.25

^aFrank (3)

CONCLUSIONS

The reaction constant for the 1-chloro-2,4-dinitrobenzene at 25° C. was $1.686 \pm .084$ liter mole⁻¹ minute⁻¹ as compared to 1.744 $\pm .080$ obtained by Frank (3). The spectrophotometric analysis (1) at the same temperature was 1.13 liter mole⁻¹ minute⁻¹. The results of this study are summarized in Table 1.

The above tables suggest the reactivity order to be Cl > Br >> I for the 1-halo-2,4-dinitrobenzene and piperidine reaction in 95% ethanol at the temperatures listed. Chapman and Parker (2) report that the 1-fluoro-2,4-dinitrobenzene reaction with piperidine in 99.8% ethanol is 50 to 100 times faster than the reaction with the chloro group.

Literature Cited

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