BY OSIAS BAIN<sup>2</sup> AND CYRIAS OUELLET

#### Abstract

A study has been made of the variation of the reaction rate constant with increasing dilution in the case of three reactions between pairs of dipolar sub-stances in ethanol solution. The reactions examined were those between aniline and 2,4-dinitrochlorobenzene, *p*-toluidine and 2,4-dinitrochlorobenzene, and p-toluidine and 2,4-dinitrobromobenzene. As the concentrations of the reactants in the first two cases are increased 50-fold, the bimolecular velocity coefficient decreases by approximately 12% in the case of the first reaction, and by 7% in the case of the second one. The rates decrease sharply as the solubility limits of the products in ethanol are approached, while they become relatively constant as high dilutions are attained.

### Introduction

In kinetics, the name given to the variation in the constants of the Arrhenius equation, viz. k, A, and E as a function of a change in initial concentration of the reactants, is the 'dilution effect'. The dilution effect has been experimentally studied and theories have been developed for ion-ion, ion-dipole, enzyme, and chain reactions, as well as for unimolecular decompositions (8). Apart from their possible significance in the interpretation of reaction mechanism and solvent effects, these dilution effects are of interest because they may have to be taken into account in the comparison of the rates of a reaction in different solvents. We are here concerned with the dilution effect in the case of reactions between two dipolar substances.

The bimolecular velocity coefficient of reactions between alkyl halides and ions in hydroxylic solvents increases as the dilution is increased, often tending to a limiting value at high dilutions which is from two to four times as great as the value found at a concentration of one gram mole per liter. Thus Hecht and Conrad (6) found that the rate of the reaction between methyl iodide and sodium ethoxide in ethanol solution at 36°C. was doubled when the dilution was increased from 2 to 100 liters per mole. Acree and Robertson (1) interpreted these phenomena in terms of the dual hypothesis and derived a relation of the type

$$k = k_m + a(k_i - k_m)$$

where  $k_i$  and  $k_m$  are the reactivities of the ion and of the undissociated molecule, and  $\alpha$  is the degree of ionization. Later workers, e.g. Mitchell (7) found that  $k_m$  was negligible in many reactions of this type, and thus concluded that the bimolecular velocity coefficient calculated on the basis of the concentration of the reactive ion rather than on the total concentration of base was independent of dilution.

Manuscript received in original form August 14, 1950, and, as revised. A pril 16, 1951. Contribution from the Department of Chemistry, Université Laval, Québec, Qué., with financial assistance from the National Research Council of Canada.

Holder of a Bursary and a Studentship under the National Research Council of Canada.

### BAIN AND QUELLET: DILUTION EFFECT

The observation of a dilution effect in a dipole-dipole reaction where a is assumed to be negligible appears to have been first made by Rheinlander (11) in 1923. Rheinlander in measuring the rates of reactions between several aromatic compounds of the type  $C_6H_3(NO_2)_2X$  with aniline and methylaniline in ethanol, observed in the case of 2,4-dinitrobromobenzene that when the concentration of the halide was kept constant and that of the base increased. the value of k diminished. When that of the halide was increased the value of kalso diminished, although more slowly. This same observation was later confirmed for analogous reactions by van Opstall (13) and by Peacock and Singh (10). The latter authors investigating the reaction between several aromatic amines and 2.4-dinitrochlorobenzene in ethanol solution found that a decrease in velocity of 20% and an increase in the energy of activation of about 500 cal. per mole was in certain cases found to attend a doubling of the concentration. The dilution effect thus measured by these authors was examined over a small range of variation of concentration and was incidental to a study of the effect of various functional groups on the reaction rate.

The present work was initiated with the view of accurately determining the dilution effect in reactions of the type examined by Peacock, and over a wide range of concentrations. Although the investigation could not be further extended, the results, in spite of their limited scope, are presented as a contribution to the experimental data on the subject.

# Experimental

Examining the rate of reaction between aniline and 2,4-dinitrochlorobenzene (I), p-toluidine and (I), and p-toluidine and 2,4-dinitrobromobenzene (II) in ethanol solution over a concentration range varying from 1 to 50 on a relative scale necessitated the use of large volumes of ethanol at the low concentrations, in order to secure a significant accuracy in the determination of k. Commercial ethanol was refluxed for several hours with silver nitrate and potassium hydroxide to remove aldehydes. In order to remove the small amount of water present an azeotropic distillation with about 15% benzene by volume was carried out. After distilling off the initial ternary azeotrope through a 30-plate bubble-cap column, the binary azeotrope benzene-ethanol was distilled off until the index of refraction of a distillate sample equalled 1.3595 for the sodium D-line at 25°C. The remaining solvent, approximately 50% by volume of the original mixture, had an index of refraction  $n_{\rm D} = 1.3595$  at 25°C., which is that of absolute ethanol at 25°C. The binary azeotrope was then utilized in removing water from a fresh sample of commercial absolute alcohol.

According to the data of Barbaudy (2), the purity of the solvent is estimated to be in excess of 99.6% ethanol, the principal impurity considered to be benzene. It is notable that both benzene and water, together and separately, raise the index of refraction of ethanol, the former linearly throughout the entire range of concentration, and the latter attaining a maximum  $n_{\rm D} = 1.3629$  at close to 80% ethanol at 25°C.

### CANADIAN JOURNAL OF CHEMISTRY. VOL. 29

Merck's acetanilide was saponified with sodium hydroxide, and the resulting aniline was steam-distilled, extracted with ether, and fractionally distilled, setting aside the first and last quarters. It was kept at all times in the dark, and coloration was very slight.

Merck's *p*-toluidine was crystallized from petroleum ether. The product melted sharply at 43.6°C., and was kept also in the dark. Eastman Kodak's 2,4-dinitrochlorobenzene was decolorized with charcoal and subsequently crystallized from a methanol-ethanol solution. The product had a melting point of 50.8°C. Brickman's 2,4-dinitrobromobenzene was crystallized from a methanol-ethanol solution, the product melting at 71.8°C.

The reactions were carried out in Kimble volumetric flasks of 100, 250, and 500 ml. capacity, suspended in a 110 liter constant-level water bath whose temperature was constant to 0.01°C. The temperature of the bath was read on a certified thermometer of the Bureau of Standards. The dilution effects were measured at 35.07°C.

Solutions of I, II, and of p-toluidine were prepared by weighing the reactants and dissolving in ethanol to the required strength in a volumetric flask. Aniline solutions were approximately prepared, and these were then volumetrically estimated by means of a titration with a standard solution of potassium bromate, by the method of Riedel (12).

A reaction was initiated by adding a determined volume of one reactant solution to a determined volume of the other, both already at the temperature of the water bath, and, as quickly as possible, followed by the adjustment of the volume to the mark with ethanol. The flask was then well agitated. The timing was started after one half of the aniline or *p*-toluidine solution had been added to the solution of the halide. Only one analysis was performed per experiment, since at high dilutions, there was relatively little product formed. Reactions were performed in duplicate and halted at from 10% (high concentration region) to 40% (low concentration region) completion.

The three reactions occurring are



The above reactions are of the second order (10, 11), following the law

$$\frac{dx}{dt} = k(a-2x) (b-x).$$

where x is the concentration in gm-ion per liter of the halide ions produced, a and b are the initial concentrations in mole per liter of the amine and the

dinitrohalobenzene respectively. According to Rheinlander (11) and Peacock and Singh (10), these reactions proceed in two steps. First one molecule of the amine attacks a molecule of the 2,4-dinitrohalobenzene forming 2,4-dinitrodiphenvlamine or 2,4-dinitro (4'-methyl) diphenvlamine plus the hydrogen halide. An additional molecule of the amine now reacts with the hydrogen halide molecule formed at a rate far greater than in the first step. The ratedetermining step is the first one.

Analyses of the halide ions produced by the reaction were performed by precipitating with silver nitrate and weighing as silver chloride or bromide. A reaction was terminated by inverting the flask containing the reaction mixture into a beaker containing dilute silver nitrate solution and a dilute solution of nitric acid, both in slight excess. The flask was then rinsed thoroughly by washing with water and benzene. It was verified that no detectable halide ions were produced from the 2,4-dinitrohalobenzene in acid aqueous medium.

In the case of the reaction between aniline and I, the molarities of the aniline solutions were approximately twice those of the solutions of I. In view of the precision sought an expanded version of the following classical equation was used:

$$k = \frac{1}{t(a-2b)} \cdot \ln\left[\frac{b(a-2x)}{a(b-x)}\right],$$
(2)

where a, b, and x are defined as above, and t is the time measured in minutes.

Expanding the logarithm term,

k

$$k = \frac{A-B}{t(a-2b)} \cdot \left[ 1 + \frac{1}{2} \left( A + B \right) + \frac{1}{3} \left( A^2 + AB + B^2 \right) + \dots \right]$$
(3)

where

 $A = \frac{a - 2b}{a - 2x}$  and  $B = \frac{a - 2b}{a}$ . If  $\frac{a}{2} = b \pm (5\% \text{ of } b)$ , then accuracy in k to five significant figures is obtained

with the first two terms of the above expansion. There results

$$= \frac{2x}{ta(a-2x)} \cdot \left[1 + \frac{(a-x)(a-2b)}{a(a-2x)}\right].$$
 (6)

In the case where  $\frac{a}{2} = b$ , the above equation reduces to

$$k = \frac{2x}{ta(a-2x)} \,. \tag{7}$$

## Results

The analytical data and the calculated values of the constant k for various initial concentrations of the reactants are given in Tables I, II, and III. In Fig. 1, *kt* is plotted vs. *t* in the case of the reaction between aniline and I, where the concentration of the former is initially 0.3218 M and that of the latter

(4), (5)

Reaction between and and are brattened about the (1)						
Anitine conc., mole/l.	I conc., mole/1.	Time, min.	AgCl weight, gm.	Flask volume, ml.	Cl ions conc., gm-ion/1.	$k$ (mean) $\times$ 10 <sup>3</sup> l.mole <sup>-t</sup> min. <sup>-t</sup>
0.006418 0.006418	$\begin{array}{c} 0.\ 003200\\ 0.\ 003200 \end{array}$	12760. 12760.	$0.0845 \\ 0.0847$	$\begin{array}{c} 500 \\ 500 \end{array}$	0.001178 0.001182	7.13
$0.07945 \\ 0.07945$	$\begin{array}{c} 0.\ 0.4000\\ 0.\ 0.4000 \end{array}$	$852.6 \\ 852.6$	$\begin{array}{c} 0.\ 4609 \\ 0.\ 4635 \end{array}$	$250 \\ 250$	$0.01286 \\ 0.01294$	7.039
0.1511 0.1511	$\begin{array}{c} 0.07700 \\ 0.07700 \end{array}$	$222.5 \\ 222.5$	$0.2115 \\ 0.2097$	100 100	$0.01476 \\ 0.01463$	7.025
$\begin{array}{c} 0.\ 2424 \\ 0.\ 2424 \end{array}$	$\begin{array}{c} 0.\ 1230 \\ 0.\ 1230 \end{array}$	$95.50 \\ 93.40$	$0.2380 \\ 0.2323$	100 100	$0.01661 \\ 0.01621$	6.732
$\begin{array}{c} 0.3278 \\ 0.3278 \end{array}$	0. 1600 0. 1600	79.45 79.45	$\begin{array}{c} 0.\ 3258 \ 0.\ 3251 \end{array}$	100 100	$\begin{array}{c} 0.02274 \\ 0.02269 \end{array}$	6.336
		1	1			1

 TABLE I

 Dilution effect

 Reaction between aniline and 2.4-dinitrochlorobenzene (I)

TABLE II

Dilution effect Reaction between p-toluidine and 2,4-dinitrochlorobenzene (I)

p-Toluidine conc., mole/l.	I conc., mole/l.	Time, nin.	AgCl weight, gm.	Flask volume ml.	Cl ions conc., gm-ion/l.	$k$ (mean) $\times 10^2$ l.mole <sup>-1</sup> min. <sup>-1</sup>
0.006400	0.003200	13256.	0.0751	250	0.002096	2.24
$0.07000 \\ 0.07000$	$\begin{array}{c} 0.03500 \\ 0.03500 \end{array}$	$696.5 \\ 696.4$	$0.2628 \\ 0.2619$	100 100	$\begin{array}{c} 0.01834 \\ 0.01824 \end{array}$	2.249
$0.1280 \\ 0.1280$	0.06400 0.06400	$350.6 \\ 350.7$	$\begin{array}{c} 0.\ 4549 \\ 0.\ 4547 \end{array}$	100 100	$\begin{array}{c} 0.03174\\ 0.03173\end{array}$	2.192
$\begin{array}{c} 0.2360 \\ 0.2360 \end{array}$	0.1180 0.1180	$145.7 \\ 133.3$	$0.7209 \\ 0.6812$	100 100	$\begin{array}{c} 0.05029 \\ 0.04752 \end{array}$	2.152
0.2800	0.1400	132.5	0.8912	100	0.06219	2.155
$\begin{array}{c} 0.\ 3200 \\ 0.\ 3200 \\ 0.\ 3200 \end{array}$	0. 1600 0. 1600 0. 1600	$135.2 \\ 86.7 \\ 77.8$	$\begin{array}{c} 1.\ 1004 \\ 0.\ 8428 \\ 0.\ 7884 \end{array}$	100 100 100	$0.07676 \\ 0.05880 \\ 0.05500$	2.109

TABLE III

Dilution effect Reaction between p-toluidine and 2,4-dinitrobromobenzene (II)

p-Toluidine conc., mole/l.	II conc., mole/l.	Time, min.	AgBr weight, gm.	Flask volume, ml.	Br ions conc., gm-ion/l.	$k$ (mean) $\times 10^2$ l.mole <sup>-1</sup> min. <sup>-1</sup>
0.07000 0.07000	$\begin{array}{c} 0.\ 03500 \\ 0.\ 03500 \end{array}$	551.2 $551.2$	$0.3766 \\ 0.3757$	100 100	0.02006 0.02001	3.467
0.1280	0.06400	215.8	0.5840	100	0.03110	3. 422
$\begin{array}{c} 0.2360 \\ 0.2360 \end{array}$	0.1180 0.1180	$114.0 \\ 105.6$	1.0501 1.0094	100 100	$\begin{array}{c} 0.05591 \\ 0.05374 \end{array}$	3.351



FIG. 1. Reaction between 0.16 M 2.4-dinitrochlorobenzene and 0.3218 M aniline in ethanol solution at 35.07°C,

0.1600 *M*. The linear curve up to 13% completion of the reaction indicates that the reaction follows the second order law up to that region. The slope of the curve, *k*, is equal to  $6.34 \times 10^{-3}$  l. mole<sup>-1</sup> min.<sup>-1</sup> for this reaction.

### Discussion

The dilution effects in the three reactions investigated are illustrated in Figs. 2, 3, and 4, where the values of k are plotted against the concentrations of the dinitrohalobenzene. It is seen that k decreases with increasing concentration. The decrease is 3.3% for a 3.4-fold increase in concentration in the case of the reaction p-toluidine-II; 6.6% for a 50-fold increase in concentration in the case of the reaction p-toluidine-I, and 11% for a 50-fold increase in concentration the case of the reaction in the case of the reaction aniline-I.

The values of k in the reactions with I level off at low concentrations where the solution tends toward ideality; they decrease sharply at the higher concentrations, where the saturation point of the 2,4-dinitrohalobenzene in ethanol is approached. However, the effects are so small that the exact forms of the curves cannot be obtained.

In principle, it is difficult to apply the second-order law in the presence of a dilution effect, since the rate constant or the activity coefficients of the reactants may be expected to vary during the course of the reaction as the con-



F1G. 2. Dilution effect in the reaction between 2,4-dinitrochlorobenzene and aniline in ethanol solution at  $35.07^{\circ}C$ .



FIG. 3. Dilution effect in the reaction between 2,4-dinitrochlorobenzene and p-toluidine in ethanol solution at  $35.07^{\circ}C$ .

BAIN AND OUELLET: DILUTION EFFECT



Fig. 4. Dilution effect in the reaction between 2,4-dinitrobromobenzene and p-toluidine in ethanol solution at 35.07°C.

centrations of the reactants decrease. However, if the dilution effects were caused by certain groups in the reacting molecules whose concentration in the medium remains constant because these groups are not destroyed in the reaction, then k would be affected by the initial concentrations only and the second-order law would hold. In our reactions, the nitro groups could play such a role. In fact, the works of Rheinlander (11) and Peacock and Singh (10) and some of our results (Fig. 1) suggest that k remains essentially constant during a reaction of the type with which we are concerned. Owing to the poor solubility of the products, our experiments at the higher concentrations, where a drift in the value of k would be detectable, had to be stopped at about 12%conversion, and the second-order law was taken as a sufficient approximation.

A dilution effect of opposite sign to the one reported here has been found by Peacock and Singh (9) for the reaction between benzyl chloride and aniline at  $35^{\circ}$  and  $40^{\circ}$ C. in ethanol. They observed a rise in the reaction rate of 29% at 35°C. and 18% at 40°C. for a doubling of the concentration. It thus appears that the roles of the solvent ethanol in this type of reaction between an aryl amine and an aryl halide are dissimilar, being dependent upon whether the halogen atom is attached directly to the benzene nucleus, although activated by two nitro groups in o-, p-positions, or whether it is attached to the benzene nucleus through a methylene group.

A theory of the dilution effects should take into account such constitutional factors together with the physical influence of dipole-dipole association, and the degrees of solvation of both the reactants and the activated complex. That dipole-swarming can lead to either a positive or a negative dilution effect is shown by Hartmann's theory (3, 4, 5) which has been applied to the reaction between pyridine and methyl iodide. For the reactions studied in this work, it seems that Hartmann's theory would predict a curvature opposite to that

shown in Figs. 2 and 3. However, the very small variations of k in our case preclude a fruitful application of Hartmann's equations since even the sign of the effect they predict depends rather critically on certain constants such as molecular radii which are not known with enough precision.

# Acknowledgments

The authors are indebted to the National Research Council for financial assistance and for a bursary to one of them (O.B.). They also wish to thank Dr. Paul-A. Giguère for his continued interest in this work.

## Résumé

On a étudié l'effet de la dilution sur la vitesse de réaction entre trois paires de substances dipolaires en solution dans l'éthanol, soient: entre l'aniline et le 2,4-dinitrochlorobenzène, la para-toluidine et le 2,4-dinitrochlorobenzène, la paratoluidine et le 2,4-dinitrobromobenzène. Dans les deux premiers cas une augmentation de concentration d'un facteur de 50 produit une diminution de la constante d'environ 12% et 7% respectivement. Pour la troisième réaction, la concentration n'a pu être augmentée que d'un facteur 3.4 à cause de la faible solubilité du 2,4-dinitrobromobenzène dans l'éthanol: il en est résulté une diminution de 3% dans la constante de vitesse. En général les constantes décroissent rapidement lorsqu'on approche la limite de solubilité des réactifs: par contre elles varient peu aux grandes dilutions.

### References

1. ACREE, S. F. and ROBERTSON, M. C. J. Am. Chem. Soc. 37: 1902. 1915.

BARBAUDY, M. J. Bull. soc. chim. France, 30: 371. 1926. HARTMANN, H. Z. Elektrochem. 47: 856. 1941. 2. 3.

HARTMANN, H. Z. physik. Chem. B, 51: 309. 1942. HARTMANN, H. Z. physik. Chem. B, 53: 37. 1943. 4.

5.

 HARIMAN, H. Z. physic Chem. D. 35, 37, 1945.
 HECHT, W. and CONRAD, M. Z. physik. Chem. 3: 450. 1889.
 MITCHELL, J. A. J. Chem. Soc. 1792. 1937.
 MOELWYN-HUGHES, A. E. The kinetics of reactions in solution. Oxford University Press. 1947. PEACOCK, D. H. and SINGH, A. J. Phys. Chem. 30: 673. PEACOCK, D. H. and SINGH, A. J. Phys. Chem. 40: 669. RHEINLANDER, A. H. J. Chem. Soc. 3090. 1923. RIEDEL, R. Z. physik. Chem. 56: 243. 1906.

9. 1926

1936. 10.

11.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by CLEMSON UNIVERSITY on 11/11/14 For personal use only.

<sup>13.</sup> VAN OPSTALL, H. J. Rec. trav. chim. 52: 901. 1933.