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THE REACTION OF UREA
WITH PRIMARY ALKYL BROMIDES

BY

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A THESIS
PRESENTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE
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ABSTRACT

The reactions between urea and the primary alkyl bromides from 1- bromobutane to 1- bromooctane were investigated. The effect of concentration, temperature, and solvents on the yield was determined. Second order reaction rate constants at temperature of 80°, 100°, and 132°C were calculated from the data for yield. The yield is defined as the percent of bromine from the alkyl bromide titrated as bromide ion.

The results indicate that the reactions of the primary alkyl bromides with urea are similar; the reaction being of the second order and the extent of reaction being approximately the same for each alkyl bromide for corresponding reaction conditions.

At a temperature of 132°C, yields of approximately 90% or greater are obtainable for reaction periods of two hours or more.

Further chemical and kinetic investigation is required in order to define the mechanism of reaction with greater certainty.

APPROVAL OF THESIS

FOR

DEPARTMENT OF CHEMICAL ENGINEERING
NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: ______________________

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NEWARK, NEW JERSEY
JUNE, 1964

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INTRODUCTION

This thesis is concerned with the reaction between urea and normal primary alkyl bromides.

The work of this thesis consists of two main parts. The first part consists of results concerning the effect of physical and chemical variables on the yield. The second part consists of a preliminary investigation of the kinetics of the reaction.

THEORY

The exact course of the reaction between the primary alkyl halides and urea is not known. However, work by Bradley (1),* indicates that the main products of the reaction are alkyl urea and dialkyl urea. The reaction between urea and 1- bromobutane would then be as follows:

(1) $NH_2CONH_2 + C_4H_9Br \dashrightarrow C_4H_9NHCONH_2 \cdot HBr + (C_4H_9)_2NCONH_2 \cdot HBr + HBr$

On adding the reaction mixture to water, the bromide ion from the HBr, the alkyl urea salt, and the dialkyl urea salt dissociates. The amount of alkyl bromide that has reacted can then be determined by volumetric titration of the bromide ion by silver nitrate solution. The unreacted alkyl bromide is insoluble in water and not dissociated.

The dialkyl urea would most likely be formed from a pair of consecutive reactions as follows:

(2) $NH_2CONH_2 + C_4H_9Br \dashrightarrow C_4H_9NHCONH_2 \cdot HBr$

(3) $C_4H_9NHCONH_2 \cdot HBr + C_4H_9Br \dashrightarrow (C_4H_9)_2NCONH_2 \cdot HBr + HBr$

From the course of the reaction proposed above, one would expect the reaction to be kinetically of the second order, and to be first order with respect to alkyl bromide and urea concentrations. One would expect reaction number (3), above, to be slower than reaction number (2). Therefore, in a reaction mixture where urea is in excess reaction number (3) would not occur to an extent great enough to affect the verification of reaction number (2) as a second order reaction using the equation:

*Refers to reference (1).

$$k = \frac{2.303}{t(a_o - b_o)} \log \frac{b_o(at)}{a_o(bt)} ,$$

to calculate the second order reaction rate constant.

When alkyl bromide is in excess, the second order reaction rate constant, calculated as above, should decrease after the time period required to carry out reaction number (2).

EXPERIMENTAL PROCEDURE

Apparatus

The reactions were carried out in test tubes inserted into 1000 milliliter, three necked, distilling flasks with 24/40 standard taper joints. Two test tubes were inserted into each flask, with asbestos cloth tape wrapped around the test tube to close the space between the test tube and the neck of the flask. A water cooled condenser tube, used as a reflux condenser, was inserted into the third neck of the distilling flask. The heating mediums, bromobenzene, chlorobenzene, water, and benzene, were placed in the distilling flasks and heated to their boiling points by use of electric heating mantles controlled by power stats. The test tube extended below the bottom of the neck of the flask by about one half of its length and thus insured that the reaction mixture was adequately heated. The mouth of the test tube was fitted with a 100 millimeter length water cooled condenser for the runs that preceded those used to obtain kinetic data. In the latter runs, an air cooled condenser, approximately two feet long, was inserted in the mouth of the test tube. The air condenser extended into the test tube about two inches. This condenser was simply a glass tube, and had a 1/4 inch hole blown out of the wall, about one inch from the bottom of the tube, so that the part of the tube in the test tube had two openings. This was done in order to prevent condensed liquid from plugging the condenser tube. A cork was used to seal the reflux condenser inlet into the test tube mouth.

Materials

The following reagents were used:

a. Urea, A.C.S. grade, Fisher Scientific Co.

b. 1- Bromobutane, 1- bromopentane, 1- bromohexane, 1- bromoheptane, 1- bromooctane, 1- bromodecane, reagent grade, Eastman Kodak Co.

The following solvents were used:

a. N,N-dimethylformamide, spectrographic grade, Matheson, Coleman, Bell Co.

b. Acetamide, reagent grade, Matheson, Coleman, Bell Co.

c. Formamide, reagent grade, Matheson, Coleman, Bell Co.

Catalyst used (two runs only):

Cupric oxide, CuO, reagent grade, Fisher Scientific Co.

Indicator used:

Eosin Yellowish, 1% Aqueous solution, reagent grade, Fisher Scientific Co., catalog no. So-E-23

Titration solution:

0.1N Silver nitrate, made from Fisher A.C.S. grade.

Standardization salt for silver nitrate:

Potassium bromide, A.C.S. grade, J. T. Baker Co.

General Procedure

The experimental work was divided into two parts. The first part, Part I, which is the work listed with numerical and alphabetical notations such as 1, 1A, 2Z2, etc., was performed to investigate the general effect of physical and chemical variables on the yield of the reaction. The second part, Part II, consists of a preliminary investigation of the kinetics of the reaction, using three different reaction mixtures - one containing 1- bromobutane, one containing 1-bromopentane, and one containing 1- bromohexane.

Part I. The material for the runs in Part I consisted of reaction mixtures that were individually made up for each test tube. Solids were weighed by difference using a weighing bottle, and were transferred to the test tube by a solids funnel - using a brush to remove any adhering material from the funnel. The alkyl bromides were weighed by difference using a small cork stoppered Erlenmeyer flask. The alkyl bromides were poured directly from the flask into the test tube. In runs 3I1, 3I2, and 3I the 1- bromohexane was measured by a weight calibrated pipet. N,N-dimethylformamide was measured by volume at 24° to 25°C (density=0.945 gm/ml), using a buret. Formamide used in run 3I3 was measured by volume using a volumetric pipet (density=1.129 g/ml at 25°C). The test tubes were fitted with a water cooled, 100 mm long, Liebig condenser used as a reflux condenser. It was observed that this arrangement will function satisfactorily if the volume of the material in the test tube is kept to about one-third of the total volume of the test tube which is about 10 ml. In runs 1, 1A, 2, 3 which were made at 155°C, some material was lost from the test tube by too rapid boiling and because too great an amount of material was placed in the test tube. Also, the urea probably decomposes at this temperature as was evidenced by a dark yellow color of the reaction mixture during and at the end of the reaction. Therefore, subsequent runs were made using about ten grams or ten ml of reaction mixture per test tube and temperatures of 132°, 100°, and 80°C. All the runs subsequent to runs 2F were made by first bringing the urea and solvent into solution and then adding the alkyl bromide. In Part I, the time of reaction is taken as the time at the indicated reaction temperature. The reactions in these runs were not immediately cooled down or stopped by removing from the distilling flask and pouring into water as were the runs used to determine kinetic data. Therefore, the former runs had some additional reaction time because of gradually cooling down to room temperature.

Part II. The material for the runs in Part II consisted of reaction mixtures containing an alkyl bromide, N,N-dimethylformamide, and urea in a single phase solution. A reaction mixture was made for each of the following: 1- bromobutane, 1- bromopentane, and 1- bromohexane, designated RM1, RM2, and RM3 respectively. The molar concentrations of the alkyl bromide, urea, and solvent were very nearly the same in each reaction mixture. The mixtures were made up by weighing the alkyl bromides and urea by difference, and measuring the volume of N,N-dimethylformamide at 24-25°C in a graduated cylinder. Densities of the reaction mixtures were measured at 20°C by a Westphal chain balance. The weight of reaction mixture transferred to the test tube at 20°C, was determined by a weight calibrated pipet. The test tubes were in place, and the heating medium was boiling before the reaction mixture was transferred to the test tube. After transferring the reaction mixture to the test tube, the two foot air cooled reflux condenser was immediately put in place in the test tube. When the desired period of reaction was completed, the test tube was removed from the distilling flask, the flask stoppered, and the reaction mixture immediately poured into approximately 30 ml of water in a 600 ml beaker. This stopped the reaction. The densities of the reaction mixtures at the reaction temperatures were determined by heating the reaction mixture in a 100 ml volumetric flask immersed in boiling heating baths of calcium chloride solutions at 95°C and 125°C. After adjusting the volume of liquid in the flask, the flask was cooled and weighed. Densities at the reaction temperatures were obtained from a graph of density versus temperature, see Tables I and II.

Table I **Experimental Densities of Reaction Mixtures, Gm./Ml**

Mixture No.	Alkyl Bromide	Temperature, °C 20	94	95	125
1	C_4	1.019	0.932	--	0.901
2	C_5	0.9991	--	0.930	0.902
3	C_6	0.9975	--	0.927	0.900

Table II **Graphically Determined Reaction Mixture Densities, Gm./Ml.**

Mixture No.	Alkyl Bromide	Temperature, °C		
		80	100	132
1	C_4	0.945	0.924	0.896
2	C_5	0.944	0.926	0.896
3	C_6	0.940	0.922	0.895

ANAYLTICAL PROCEDURE

The only analysis performed on the reacted mixtures was a volumetric titration for bromide ion.

The method for the analysis of bromide ion is given in reference (2), page 544. A 0.1% aqueous solution of eosin yellowish (sodium tetrabromfluoresceinate) was used as the indicator. The end point of the titration is indicated by a rapid color change from a faint pink tint or no tint, to an intense pink or reddish pink color, depending on the concentration of bromide ion and reaction mixture titrated. The lower alkyl bromides, such as butyl and pentyl, give darker end points, and lower concentrations of bromide ion (lower yields) give darker end points than solutions with higher concentrations of bromide ion.

In Part I, for all runs except runs J, the following procedure was used:

a. The contents of the test tube was diluted to 500 ml in a volumetric flask.

b. 50 ml of this solution was added to a 250 ml Erlenmeyer Flask using a 50 ml pipet, and 3 ml of 6N acetic acid was added.

c. 10 to 14 drops of 0.1% eosin yellowish indicator solution was used.

d. The solution was titrated with 0.10 silver nitrate solution to a pink end point.

In runs J, the procedure was the same, except that the contents of the test tube were diluted to 200 ml and 50 ml of this solution was then titrated.

In Part II, for Reaction Mixture 1-80°, 100°, 132°, and RM2, RM3-132°C runs, the material in the test tube was diluted to 100 ml, and 50 ml ml of this solution was titrated after adding 50 ml of distilled water, 4 ml of 6N acetic acid, and 14 drops of eosin indicator, For RM2 and RM3, 80° and 100°C runs, the contents of the test tube was diluted to 200 ml in a 600 ml beaker, 8 ml of 6 N acetic acid and 28 drops of eosin yellowish was added, and the solution was titrated with 0.1N silver nitrate solution.

The use of a magnetic stirrer aids in speeding the titration and observing the end point. A magnetic stirrer was used in Part II, and Part I, runs H, I, and J.

The concentration of the bromide ion in the solutions that were titrated was kept by the foregoing procedure, within 0.001 and 0.05 moles per liter, the outer limits of reliability for this analysis: see page 453 and 544, reference (2).

The titrations are reproducible, for the same solution, to well within 1% average deviation.

SAMPLE CALCULATIONS

Calculation of Second Order Reaction Rate Constant

The rate constant is calculated for the following reaction:

Urea + n- alkyl bromide $\longrightarrow$ Products, or A + B $\longrightarrow$ Products

The following quantities were used:

a_i = urea concentration, moles/liter, as solution is originally formulated

a_o = urea concentration, moles/liter, at "adopted time" zero, 30 minutes after start of reaction

a_t = urea concentration, moles/liter, at time t; b_i, b_o, b_t are corresponding alkyl bromide concentrations

k = second order reaction rate constant, liter/mole-min.

N = normality of silver nitrate solution

t = "adopted time", t is taken as zero, 30 minutes after start of reaction, minutes

V_o = volume of silver nitrate solution used at t = 0, per total mixture in test tube, ml

V_s = volume of reaction mixture in test tube at reaction temperature, ml

V_t = volume of silver nitrate solution used at time t, per test tube, ml

x = moles of alkyl bromide reacted per liter at time t, equal to NV_t/V_s

In the calculation of k, t is taken as beginning 30 minutes from the actual start of the reaction. Therefore, a_i must be adjusted to correspond to this "adopted time".

Accordingly:

$a_o = a_i - x = a_i - (NV_o/V_s)$,

$b_o = b_i - x = b_i - (NV_o/V_s)$.

The variable concentration terms are calculated as follows:

$$a_t = a_i - (NV_t/V_s),$$

$$b_t = b_i - (NV_t/V_s).$$

Therefore,

$$k = \frac{2.303}{t(a_o - b_o)} \log \frac{b_o a_t}{a_o b_t}.$$

For the reaction mixture containing 1- bromobutane (RM1) at 80°C:

$$a_i = 0.01379 \text{ moles}/10.5 \text{ ml} \times 1000\text{ml}/1 = 1.311 \text{ mole}/1$$

$$b_i = 0.00599 /10.5 \times 1000 = 0.571 \text{ mole}/1$$

$$a_o = 1.311 - (0.0986 \times 15.68/10.5) = 1.164 \text{ mole}/1$$

$$b_o = 0.571 - (0.0986 \times 15.68/10.5) = 0.424 \text{ mole}/1$$

$$k = \frac{2.303}{t\ (1.164 - 0.424)} \log \frac{0.424\ (1.311 - (0.0986 \times V_t/10.5))}{1.164\ (0.571 - (0.0986 \times V_t/10.5))}$$

$$k = (3.11/t) \log (0.364\ (139.8 - V_t)/(60.8 - v_t)).$$

At $t = 60$ min:

$$k = (3.11/60) \log (0.364(139.8-17.3)/(60.8-17.3))$$

$$k = 5.56 \times 10^{-4} \text{ 1/mole-min}.$$

See Table III for equations used to calculate k.

<u>Calculation of a_i.</u> The following quantities are used:

n_i = millimoles of urea per test tube

w = weight of reaction mixture delivered by 10 ml pipet at 20°C, grams

p = weight fraction of urea in reaction mixture

M = molecular weight of urea

Therefore,

$$n_i = w \times p \times 1000/M.$$

Table III **Equations for Calculating k**

RM1:

$$80^{o}C, \; k = \frac{3.11}{t} \; \log \; \frac{0.364(139.8 - V_t)}{(60.8 - V_t)}$$

$$100^{o}C, \; k = \frac{3.19}{t} \; \log \; \frac{0.415(139.8 - V_t)}{(60.7 - V_t)}$$

$$132^{o}C, \; k = \frac{3.28}{t} \; \log \; \frac{0.254(139.8 - V_t)}{(60.7 - V_t)}$$

RM2:

$$80^{o}C, \; k = \frac{3.10}{t} \; \log \; \frac{0.390(138.4 - V_t)}{(59.7 - V_t)}$$

$$100^{o}C, \; k = \frac{3.16}{t} \; \log \; \frac{0.376(138.8 - V_t)}{(59.6 - V_t)}$$

$$132^{o}C, \; k = \frac{3.28}{t} \; \log \; \frac{0.262(138.9 - V_t)}{(59.8 - V_t)}$$

RM3:

$$80^{o}C, \; k - \frac{3.12}{t} \; \log \; \frac{0.390(137.4 - V_t)}{(59.3 - V_t)}$$

$$100^{o}C, \; k = \frac{3.18}{t} \; \log \; \frac{0.378(137.8 - V_t)}{(59.3 - V_t)}$$

$$132^{o}C, \; k = \frac{3.30}{t} \; \log \; \frac{0.272(137.9 - V_t)}{(59.4 - V_t)}$$

Table IV **Equations for Calculating Yield for Kinetic Data**

RM1:

$\%\ \text{Yield} = 1.648\ V_t$

RM2:

At 80° and 100°C -

$\%\ \text{Yield} = 1.678\ V_t$

At 132°C

$\%\ \text{Yield} = 1.671\ V_t$

RM3:

At 80° and 100°C

$\%\ \text{Yield} = 1.689\ V_t$

At 132°C

$\%\ \text{Yield} = 1.682\ V_t$

For RM1:

$n_i = 9.95 \times 0.0833 \times 1000/60.06 = 13.79.$

Calculation of b_i. This calculation is analogous to that for a_i.

Calculation of Yield

Yield is defined as the percent of total bromine from alkyl bromide titrated as bromide ion. The following quantities are used:

V_t = volume of silver nitrate solution used, ml

N = normality of silver nitrate solution

r = No. of millimoles per milliequivalent of bromide

m_i = millimoles of alkyl bromide per test tube

$$\% \text{ yield} = V_t \times N \times r \times 100/m_i$$

For RM1 at 80°C, and t = 60 min:

$$\% \text{ yield} = 17.30 \times 0.0986 \times 1 \times 100/5.99$$

$$\% \text{ yield} = 28.4$$

See Table IV for equations used to calculate yield in Part II.

Calculation of Energy of Activation

The energy of activation is calculated from the slope of the Arrhenius equation:

$$\log_{10} k = (-DE^*/4.58)\,(1/T) + C,$$

where $(-DE^*/4.58) = \dfrac{\log_{10}(k_2/k_1)}{1/T_2 - 1/T_1} = \text{slope}$

The symbols are defined as follows:

C = a constant (not used in this calculation)

DE^* = energy of activation, calories per gm-mole

k = reaction rate constant, $\text{l-mole}^{-1} - \text{min}^{-1}$
k_2 is taken at 353 °K, k, is taken at 405K

T = absolute temperature, $^{\circ}K$, T_2 is taken as $353^{\circ}K$ and T_1 as $405^{\circ}K$

<u>DE^* for 1- bromobutane and urea (RM1)</u>.

$$\text{slope} = \frac{\log_{10}(0.765 \times 10^{-3}/11.4 \times 10^{-3})}{(1/353) - (1/405)}$$

slope = 3180.

Therefore, $DE^* = 4.58\ (-3180) = 14570$ calories.

DISCUSSION OF RESULTS

Since the experimental work was performed in two parts, the results obtained in each part will be discussed separately.

Part I

The results obtained in this phase are from reaction mixtures that contained varying quantities of urea and alkyl bromide. Urea was used in excess in all of the runs. Comparison of the runs, listed in Tables V through XIII, may be made by comparing the runs with approximately equal urea to alkyl bromide mole ratios. Many of the reaction mixtures resulted in two phase systems; mostly two liquid phases. However, the two phase data do indicate consistent effects resulting from changes in reaction variables.

1- Bromobutane. The only reliable result for 1- bromobutane in this part shows a yield of 44.7% at 100°C, urea to bromide ratio of 2.76, and urea concentration of 10.93 mole% (Run 1J). DMFA (N,N-dimethylformamide) was the solvent, and the reaction time was two hours.

1- Bromopentane. In two sets of runs at 80°C, runs 2F and 2G, the yield increased with increasing mole ratio of urea to 1- bromopentane. In runs 2F the concentration of 1- bromopentane was kept constant at about 5 mole %. In runs 2G the mole % of urea was constant at about 23% and the mole ratio of DMFA to urea was constant at about 3.1. There was no observable effect on the yield vs. urea/alkyl bromide mole ratio relationship due to the two sets of conditions.

Table V **Effect of Solvent Ratio on Yield for 1-Bromopentane Reactions**

Run	Urea Conc., Mole %	C_5 Conc. Mole %	Mole Ratio, DMFA Urea	Yield %
2F	11 to 40	5	8 to 1.4	17.5-33.9
2G	23	3.8 to 6	3.1	28.4-35.0

Table VI **Formulations for 1- Bromobutane Reactions**

Run No.	Urea			1- Bromobutane			Solvent			
	wt. gram	moles	mole %	wt. gram	moles	mole %	Name	wt. grams	moles	volume ml
1	10.45	0.1740	47.0	3.955	0.2887	7.81	acetamide	9.90	0.1676	---
1A	5.654	0.0941	45.9	4.192	0.0306	14.92	"	4.737	0.0802	---
1J	1.057	0.01758	10.93	0.872	0.00636	3.91	DMFA	9.99	0.1367	10.58

Table VII **Yield for 1- Bromobutane Reactions**

Run No.	Ratio: Mole Urea / mole C_4	Molality C_4 in Solvent	Reaction Time, min.	Temp. °C	Yield %	Phase(s)
1 *	6.02	2.89	610	155	31.8	liq.
1A *	3.08	6.46	625	155	43.8	liq.
1J	2.76	0.637	120	100	44.7	liq.

* 1- Bromobutane lost by vaporization

Table VIII **Formulations for 1- Bromopentane Reactions**

Run No.	Urea		-	1- Bromopentane		-	Solvent			
	wt. gm.	moles	mole %	wt. gm.	moles	mole %	Name	wt. gm.	moles	Volume ml.
2	10.40	0.1731	46.2	4.479	0.02965	7.92	Acetamide	10.18	0.1723	---
2A	4.768	0.07939	41.9	4.097	0.02713	14.27	"	4.904	0.0830	---
2C1	4.891	0.0814	37.4	1.600	0.01059	4.85	DMFA	9.18	0.1256	9.72
2C2	5.129	0.0853	36.8	3.106	0.02056	8.88	"	9.23	0.1261	9.76
2D1	5.188	0.0863	38.5	1.514	0.01002	4.48	"	9.36	0.1280	9.91
2D2	5.321	0.0886	37.2	2.978	0.01972	8.30	"	9.45	0.1292	10.00
2E1	4.937	0.0821	36.5	1.651	0.01092	4.86	"	9.62	0.1316	10.18
2E2	5.167	0.0860	36.6	3.090	0.0204	8.68	"	9.44	0.1289	9.98
2J	0.989	0.01648	10.32	0.958	0.00634	3.97	"	10.0	0.1368	10.62
2F2	1.276	0.0212	10.62	1.423	0.00942	4.72	"	12.33	0.1688	13.06
2F4	2.348	0.0391	19.60	1.485	0.00982	4.92	"	11.01	0.1507	11.64
2F6	3.560	0.0593	29.8	1.475	0.00976	4.89	"	9.52	0.1302	10.08
2F8	4.848	0.0806	40.3	1.498	0.00991	4.95	"	8.02	0.1097	8.48

Table VIII cont'd.

Run No.	Urea			- 1- Bropentane -			Solvent			
	wt. gm.	moles	mole %	wt. gm.	moles	mole %	Name	wt. gm.	moles	Volume ml.
2G1	2.57	0.0428	23.4	1.035	0.00685	3.75	DMFA	9.74	0.1331	10.30
2G2	2.54	0.0423	23.3	1.244	0.00824	4.54	"	9.56	0.1310	10.12
2G3	2.52	0.0419	23.0	1.490	0.00986	5.41	"	9.54	0.1306	10.10
2G4	2.55	0.0424	22.8	1.742-	0.01153	6.19	"	9.68	0.1323	10.24
2H1	1.209	0.0201	10.10	1.509	0.00999	5.01	Acetamide	9.99	0.169	---
2H2	4.85	0.0806	40.4	1.525	0.0101	5.06	"	6.45	0.109	---
2H3	2.56	0.0426	22.7	1.786	0.01181	6.31	"	7.87	0.133	---
2H4	2.60	0.0433	23.7	1.088	0.00720	3.94	"	7.83	0.132	---

Table IX **Yield for 1- Bromopentane Reactions**

Run. No.	Ratio: mole urea/mole C_5	Molality C_5 in Solvent	Reaction Time, min.	Temp. °C	Yield %	Phase(s)
2	5.83	2.92	610	155	62.5	liq.
2A*	2.93	5.53	625	155	95.2	liq, liq.
2C1	7.69	1.152	320	132	97.4	liq, liq.
2C2	4.14	2.23	320	132	97.0	liq, liq.
2D1	8.59	1.07	90	100	49.5	liq, sol.
2D2	4.49	2.09	90	100	36.6	liq, sol.
2E1	7.51	1.136	302	100	82.8	liq.,sol.
2E2	4.21	2.16	302	100	70.1	liq.,sol.
2J	2.60	0.634	120	100	44.5	liq.
2F2	2.25	0.764	120	80	17.5	"
2F4	3.98	0.811	120	80	24.0	"
2F6	6.07	1.024	120	80	29.9	"
2F8	8.14	1.236	120	80	33.9	"
2G1	6.25	0.704	120	80	35.0	"
2G2	5.14	0.861	120	80	33.0	"
2G3	4.25	1.033	120	80	31.0	"
2G4	3.67	1.192	120	80	28.4	"
2H1	2.01	1.000	120	80	10.4	liq.,liq.
2H2	7.99	1.565	120	80	11.2	liq.,liq.
2H3	3.60	1.500	120	80	9.59	liq.,liq.
2H4	6.01	0.920	120	80	20.8	liq.,liq.

* CuO catalyst used, 0.0308 mole/mole C_5.

Table X **Formulations for 1- Bromohexane Reactions**

Run No.		Urea	-		1- Bromohexane	-		Solvent		
	wt. gm.	moles	mole %	wt. gm.	moles	mole %	Name	wt. gm.	moles	Volume ml.
3	10.45	0.1740	46.0	5.028	0.0305	8.06	acetamide	10.23	0.1732	---
3A*	4.622	0.07696	40.9	4.725	0.0286	15.21	"	4.859	0.0823	---
3B	4.929	0.08207	42.2	4.844	0.0293	15.1	DMFA	6.06	0.0829	6.41
3C1	4.907	0.0817	37.2	1.630	0.00990	4.51	"	9.35	0.1279	9.90
3C2	5.506	0.0917	38.3	3.328	0.0202	8.42	"	9.35	0.1279	9.90
3D1	4.784	0.0795	36.8	1.307	0.00791	3.66	"	9.41	0.1288	9.96
3D2	4.679	0.0779	34.7	2.918	0.01766	7.85	"	9.44	0.1290	9.98
3E1	4.922	0.0818	36.9	1.743	0.01057=	4.76	"	9.49	0.1295	10.02
3E2	4.6831	0.0778	34.3	3.260	0.01973	8.69	"	9.46	0.1292	10.00
3I1	1.012	0.01688	10.40	1.056	0.00639	3.94	"	10.15	0.1388	10.73
3I2	1.043	0.01739	8.97	1.056	0.00639	3.30	acetamide	10.05	0.170	---
3I3	1.015	0.01690	6.82	1.056	0.00639	2.58	formamide	10.12	0.225	8.97
3J	1.024	0.01706	10.68	0.992	0.00603	3.77	DMFA	10.0	0.1368	10.59

* CuO catalyst used, 0.0367 mole/mole C_6

Table XI **Yield for 1- Bromohexane Reactions**

Run No.	Ratio: mole urea / mole C_6	Molality C_6 in Solvent	Reaction time, min.	Temp. °C	Yield %	Phase(s)
3	5.70	2.98	610	155	80.0	liq.
3A*	2.69	5.89	625	155	93.6	liq.,liq.
3B	2.80	4.83	300	155	97.9	" "
3C1	8.28	1.056	320	132	85.9	" "
3C2	4.54	2.16	320	132	53.8	" "
3D1	10.04	0.841	90	100	48.6	liq.,sol.
3D2	4.41	1.872	90	100	27.2	" "
3E1	7.74	1.112	300	100	80.4	" "
3E2	3.94	2.08	300	100	60.3	" "
3I1	2.64	0.630	120	100	43.0	liq.
3I2	2.72	0.636	120	100	24.5	"
3I3	2.64	0.632	120	100	16.8	"
3J	2.84	0.601	120	100	46.4	"

* CuO catalyst used, 0.0367 mole/mole C_6.

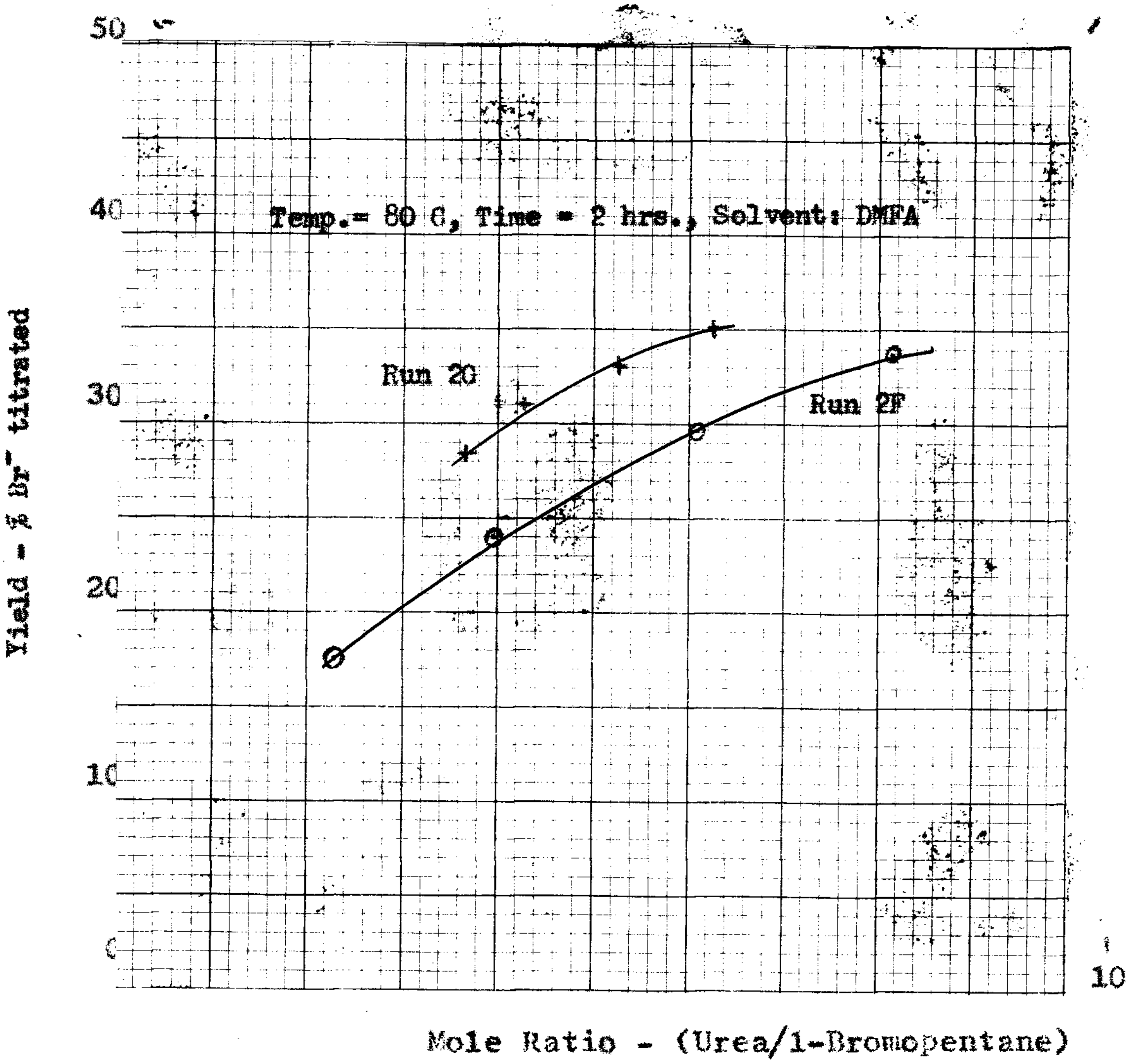

Figure 1. Yield versus Mole Ratio Urea to 1-Bromopentane

The apparent difference in yield indicated in Fig. 1, and in Table V was caused by the fact that the urea was not totally dissolved in the DMFA before the addition of the 1- bromopentane in the 2F runs. The urea was totally dissolved at about one hour after the start of the run.

The yield for a single phase system at 100°C, 2.60 mole ratio, and reaction time of 120 min. was 44.5%. At 80°C, 6.25 mole ratio, and a reaction time of 120 min. the yield was 35.0%. (See runs 2J and 2G1.) The data for both single and two phase systems indicate that yield increases with increasing urea/ 1- bromopentane mole ratio, temperature, and reaction time. The reaction is unaffected by the mole ratio of solvent to urea using DMFA.

In runs 2H acetamide was used as the solvent. A two phase liquid-liquid system resulted giving lower yields than those obtained in DMFA at the same urea/1- bromopentane mole ratios.

The highest yield obtained was 97.4%, in a two phase liquid-liquid system using DMFA, at 131°C, 320 min. reaction time, and at a mole ratio of 7.69 (run 2C1).

<u>1- Bromohexane.</u> The data indicate that an increase in urea/1-bromohexane mole ratio, reaction time, and temperature results in an increase in yield.

In runs 3I solvents were compared. In single phase systems the yields using formamide, acetamide, and DMFA were 16.8%, 24.5%,

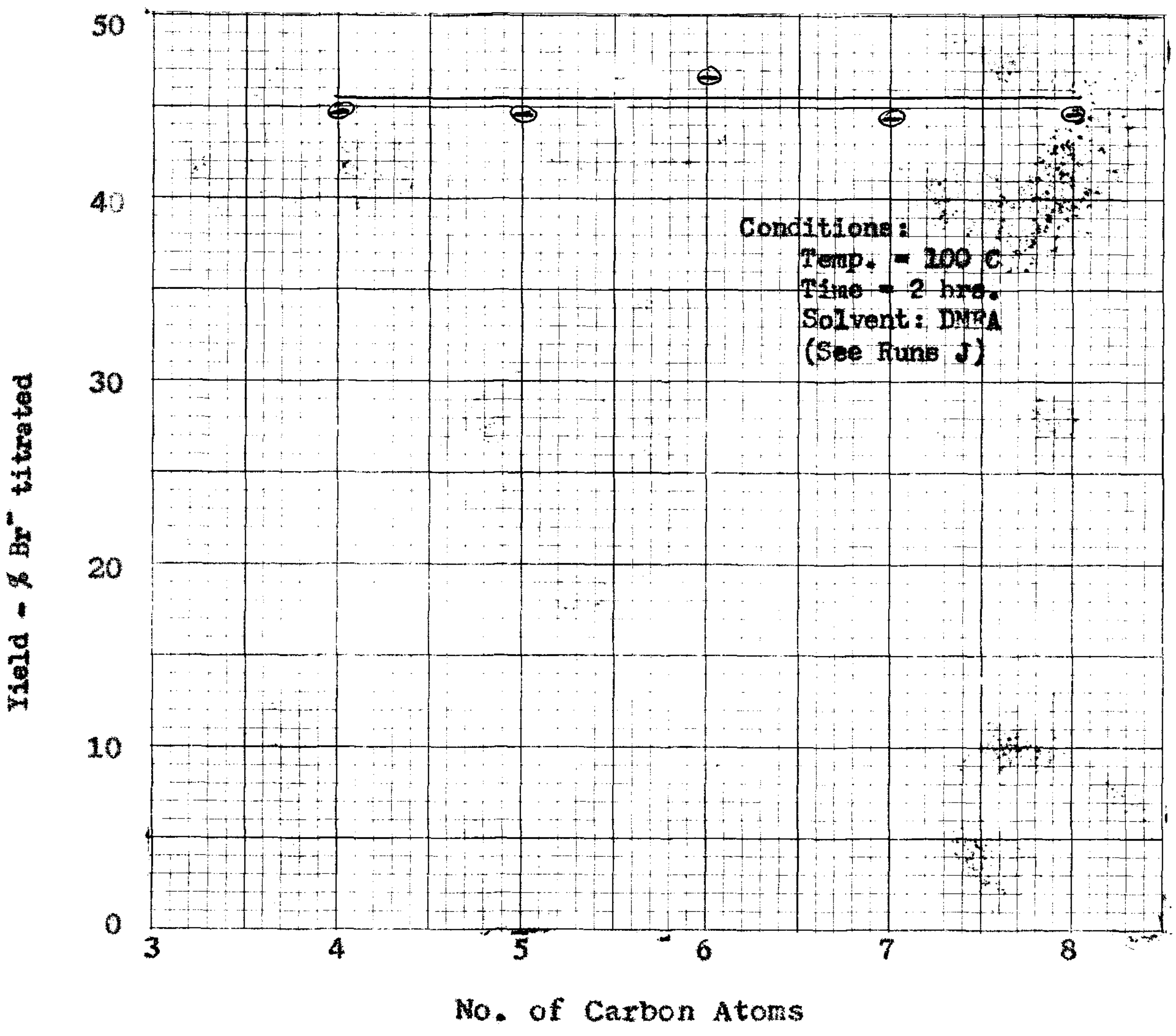

Figure 2. Yield versus Number of Carbon Atoms in Primary Alkyl Bromide

Table XII **Effect of No. C Atoms on Yield**

Run No.	Ratio: mole urea / mole C_x	Molality C_x in DMFA	Reaction Time, min.	Temp. °C	Yield %	Phase(s)
1J	2.76	0.637	120	100	44.7	liq.
2J	2.60	0.634	120	100	44.5	"
3J	2.84	0.601	120	100	46.4	"
4J	2.69	0.611	120	100	44.1	"
5J	2.65	0.628	120	100	44.7	"
7J*	2.75	0.615	120	100	---	"

* End point not obtained in titration.

Table XIII **Formulations for Runs J**

Run No.	Urea	-		Alkyl Bromide		-	Solvent			
	wt. gm.	moles	mole %	wt. gm.	moles $x10^3$	mole %	Name	wt. gm.	moles	Volume ml.
1J	1.057	0.01758	10.93	0.872	6.36	3.96	DMFA	9.99	0.1367	10.58
2J	0.989	0.01648	10.32	0.958	6.34	3.97	"	10.0	0.1368	10.62
3J	1.024	0.01706	10.68	0.992	6.01	3.77	"	10.0	0.1368	10.59
4J	0.987	0.01642	10.31	1.093	6.11	3.84	"	10.0	0.1368	10.59
5J	0.998	0.01661	10.41	1.213	6.28	3.94	"	10.0	0.1368	10.60
7J	1.014	0.01690	10.58	1.360	6.15	3.85	"	10.0	0.1368	10.60

and 43.0% respectively for a mole ration of urea/1- bromohexane of about 2.65, 0.63 molality of 1- bromohexane in solvent, reaction time of 120 min., and a temperature of 100C.

The highest yield obtained was 97.9% (Run 3B) at 155 C, 2.80 mole ratio, reaction time of five hours, and using DMFA solvent.

Effect of Chain Length on Yield

In runs J, butyl, pentyl, hexyl, heptyl, octyl, and decyl bromides were reacted. The yield as shown in Table XII, and Fig. 2, was unaffected by the number of carbon atoms in the straight chain alkyl halide. The yield was about 45% for each alkyl halide up to octyl. The yield for 1- bromodecane was not obtained because the end point was not found during the titration. This effect of chain length is expected from knowledge of alkyl halide reactions. It is known that in the reactions of primary normal alkyl halides with nucleophilic reagents that the higher alkyl homologs react at about the same rate. See reference (3), pages 23 and 24.

Solvents

N,N-dimethylformamide was found to be the best solvent, as shown by runs 3I for 1- bromohexane and runs 2F, 2G, and 2H for 1- bromopentane. This solvent can dissolve 1.52 grams of urea per ml at 100°C or 161 parts by weight of urea per 100 parts of DMFA. 1- bromobutane, 1-bromopentane, 1- bromohexane, and 1- bromoheptane were found to be soluble in DMFA in all proportions at 100°C and at room temperature. However, when DMFA, urea, and alkyl bromide are mixed two phase systems may result; see Tables IX and XI. The urea and alkyl bromide must be kept below certain limiting concentrations in order to produce one phase systems. The exact limits have not been established by these data.

At 80°C a one phase system is obtained with a 8.14 mole ratio of urea/1- bromopentane, 1.24 molality of bromide in DMFA, 40.3% mole concentration of urea, and a 4.95 mole % concentration of 1- bromopentane. Simultaneous concentrations of urea and alkyl bromide approaching or higher than 40 and 8 mole % respectively are likely to result in two phase systems at temperatures below 155°C.

Part II.

The results in this part were used to calculate the second order reaction rate constants for 1- bromobutane, 1- bromopentane and 1-bromohexane reactions with urea. All results are for single phase systems. Formulations are listed in Table XIV. Test tube quantities are listed in Table XVIII. The percent yield versus reaction time curves are shown in Figs. 3, 4, and 5. All three reactions exhibited similiar variation of yield versus time. The second order reaction rate constants as indicated in Tables XV, XVI, and XVII, are of the same order of magnitude at each temperature, for each compound investigated.

In Figure 3, for 1- bromobutane, the 80°C, curve exhibits an unusual and unexpected increase in reaction rate with time near the end of the reaction period. This may have been caused by a loss of 1- bromobutane through vaporization, thereby increasing the urea/1- bromobutane mole ratio, and thus causing an increase in reaction rate.

The more exact determination of yield versus time in Part II verifies the data from Part I concerning the variation of yield with number

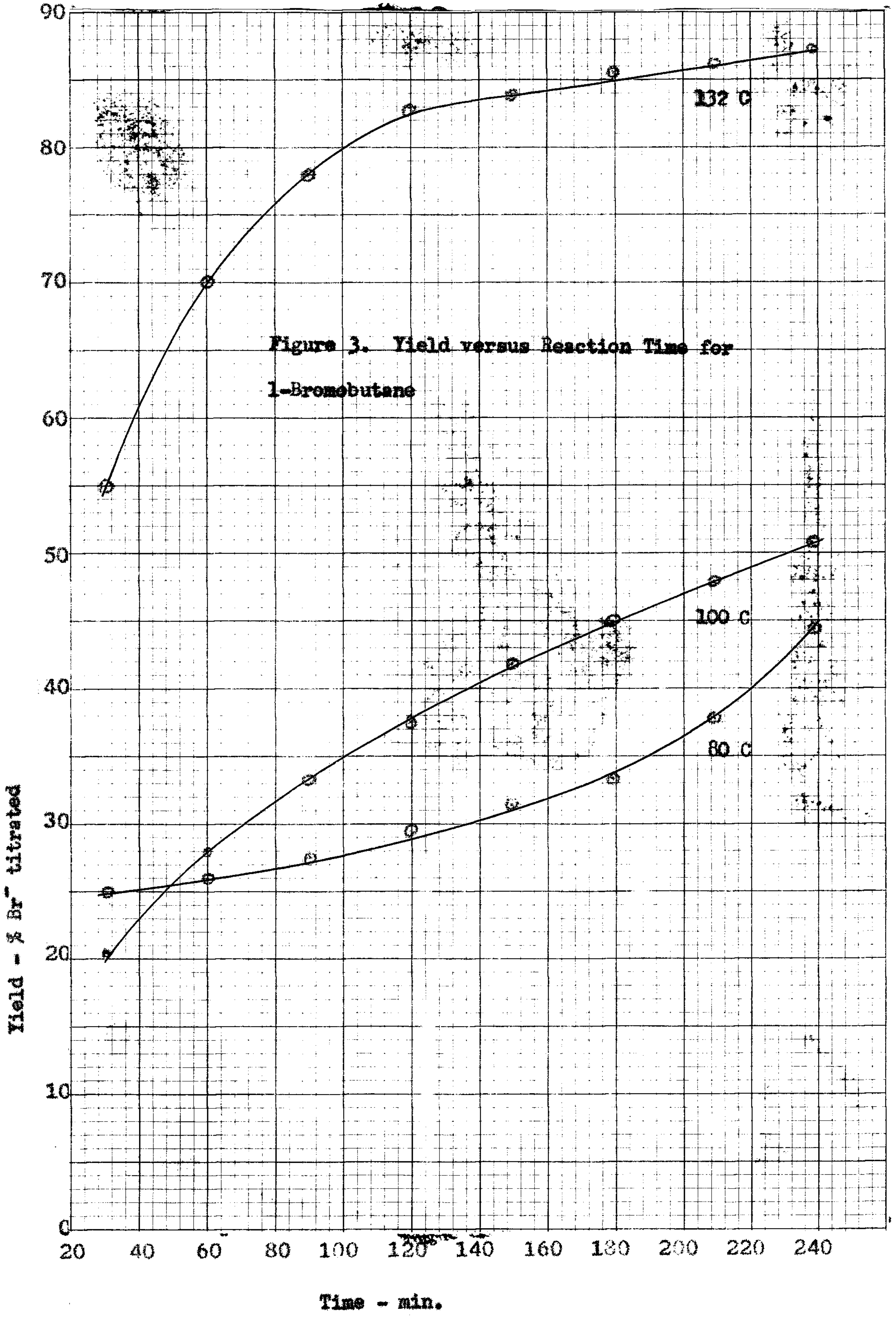

Figure 3. Yield versus Reaction Time for 1-Bromobutane

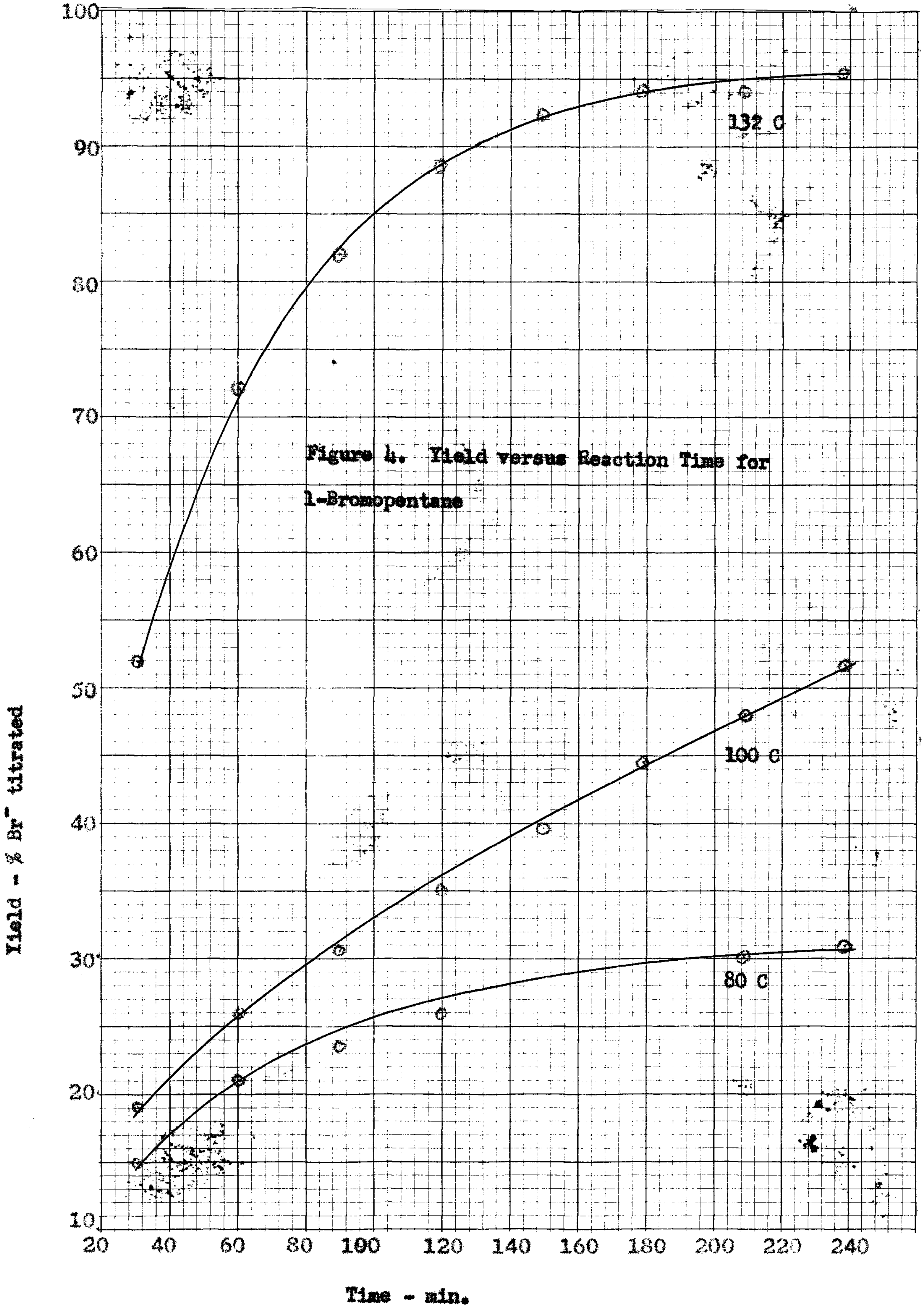

Figure 4. Yield versus Reaction Time for 1-Bromopentane

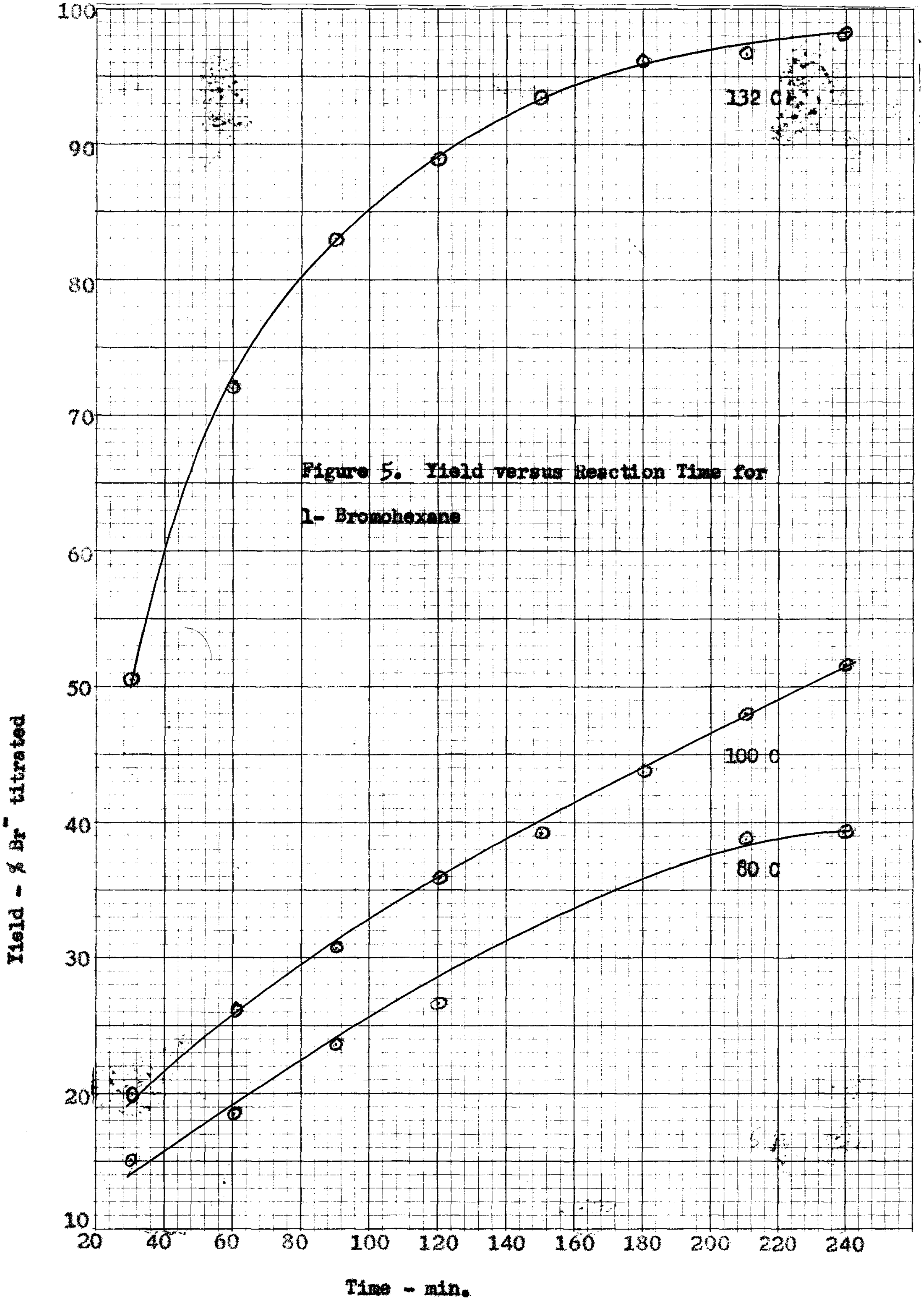

Figure 5. Yield versus Reaction Time for 1- Bromohexane

of carbon atoms in the alkyl bromide. Fig. 2, from Part I shows that yield is nearly the same for each alkyl bromide up to octyl at 100°C, and the same result is obtained at 100° and 132°C for the three compounds used in Part II.

Table XIV **Formulation of Reaction Mixtures Used in Kinetic Study**

Mixture No.:	Compound	Weight, gms.	Moles	Weight, %	Moles, %	Molality RBr in DMFA	Mole Ratio urea/RBr
1							
	Urea	49.97	0.831	8.33	10.35		2.30
	C_4H_9Br	49.53	0.361	8.25	4.49	0.721	
	DMFA	501.0	6.85	83.4	85.2		
2							
	Urea	50.00	0.832	8.28	10.38		2.32
	$C_5H_{11}Br$	54.26	0.359	8.99	4.47	0.718	
	DMFA	500.0	6.84	82.73	85.15		
3							
	Urea	50.05	0.833	8.21	10.38		2.31
	$C_6H_{13}Br$	59.52	0.360	9.78	4.49	0.720	
	DMFA	500.0	6.84	82.0	85.1		

Table XV Yield and Second Order Reaction Rate Constants, 1- Bromobutane (RM1)

Adopted Time, min.	80, °C			100, °C			132, °C		
	Vt, ml	Yield, %	kx10^4 1/mole-min	Vt, ml	Yield %	kx10^4	Vt, ml	Yield %	kx10^4
0	15.68	25.8	-----	12.96	21.3	----	33.92	55.8	----
30	16.34	26.9	4.48	17.36	28.6	73.6	43.24	71.1	160
60	17.30	28.4	5.56	20.80	34.2	49.4	48.08	79.0	146
90	18.48	30.4	6.62	23.32	38.4	39.4	51.04	83.9	133
120	19.64	32.3	6.76	25.96	42.7	35.2	51.68	84.9	109
150	20.80	34.2	7.11	27.84	45.8	31.7	52.56	86.5	95.5
180	23.52	38.7	9.59	29.60	48.7	29.7	53.04	87.2	83.0
210	27.60	45.4	13.4	31.40	51.6	28.4	53.52	88.2	74.9

Table XVI <u>Yield and Second Order Reaction Rate Constant, 1- Bromopentane (RM2)</u>

Adopted Time, min.	80, °C			100, °C			132, °C		
	Vt, ml	Yield, %	$k \times 10^4$ 1/mole-min.	Vt, ml	Yield %	$k \times 10^4$ 1/mole-min	Vt, ml	Yield, %	$k \times 10^4$ 1/mole-min
0	9.30	15.6	------	11.90	19.97	-----	31.60	52.9	-----
30	12.96	21.7	21.1	15.88	26.6	24.9	43.60	73.0	205
60	14.36	24.1	14.8	18.62	31.4	22.4	49.60	83.0	197
90	15.86	26.6	12.9	21.44	35.9	22.2	53.56	89.5	202
120	----	----	----	24.14	40.4	22.2	55.80	93.3	202
150	----	----	----	27.04	45.3	23.2	56.86	95.0	189
180	18.44	30.9	9.25	29.12	48.8	22.9	56.72	94.5	153
210	18.82	31.6	8.40	31.34	52.5	23.4	57.56	96.3	154

Table XVII Yield and Second Order Reaction Rate Constant, 1- Bromohexane (RM3)

Adopted Time, min.	80, °C			100 °C			132 °C		
	Vt, ml	Yield, %	kx10^4 1/mole-min	Vt, ml	Yield %	kx10^4 1/mole-min	Vt, ml	Yield, %	kx10^4 1/mole-min
0	9.00	15.29	-----	11.84	20.0	-----	30.12	50.6	-----
30	11.08	18.69	9.38	15.58	26.3	26.0	42.96	72.2	216
60	14.00	23.6	13.58	18.30	30.9	22.2	49.48	83.1	214
90	15.74	26.6	12.70	21.30	36.0	22.8	52.92	89.0	202
120	----	----	----	23.24	39.2	20.9	55.60	93.6	212
150	----	----	----	25.96	43.8	22.0	57.12	96.1	216
180	23.05	38.9	15.71	28.44	48.0	22.5	57.44	96.6	191
210	23.20	39.2	13.58	30.60	51.6	22.8	58.44	98.3	210

Table XVIII **Test Tube Quantities Used in Kinetic Study**

Mixture No.	Alkyl Bromide	Weight, gms.	Volume, ml		
			80°C	100°C	132°C
1	C_4	9.953	10.5	10.8	11.1
2	C_5	9.928	10.5	10.7	11.1
3	C_6	9.910	10.5	10.7	11.1

Table XIX Engergy of Activation and Average Second Order Reaction Rate Constants*

1-mole^{-1}-min^{-1}

Temp. °C	80°	100°	132°	DE, kcal/mole
RM1	$(0.765 \pm 0.220)10^{-3}$	$(3.56 \pm 0.58)10^{-3}$	$(11.4 \pm 2.7)10^{-3}$	14.57
RM2	$(1.13 \pm 0.25)10^{-3}$	$(2.30 \pm 0.07)10^{-3}$	$(18.6 \pm 1.8)10^{-3}$	15.03
RM3	$(1.30 \pm 0.16)10^{-3}$	$(2.27 \pm 0.10)10^{-3}$	$(20.9 \pm 0.7)10^{-3}$	14.92

* Average value ± average deviation.

Energy of Activation

The energy of activation for the reaction of each compound in Part II is listed in Table XIX. The small variation in the value of the energy of activation supports the assumption that the reactions of these compounds with urea are similar.

CONCLUSIONS

1. The yield increases with increasing (urea/alkyl bromide) mole ratio, temperature, and reaction time.

2. N,N-dimethylformamide is the better solvent when compared to acetamide and formamide. Its use results in higher yields and it is able to dissolve greater amounts of urea and alkyl bromide simultaneously.

3. The yield is unaffected by the mole ratio of solvent to urea or solvent to alkyl bromide in single phase systems, all other conditions being equal.

4. The normal primary alkyl bromides, from butyl to octyl, all react at nearly the same rate under the conditions investigated.

5. The second order reaction rate constants for the reactions of 1-bromobutane, 1- bromopentane, and 1- bromohexane with urea are the same order of magnitude at the temperatures of 80°, 100°, and 132°C.

6. The values of the energy of activation for the 1- bromobutane, 1-bromopentane, and 1- bromohexane reactions are nearly the same, varying from 14.57 to 15.03 kilocalories per mole.

7. The reaction is of the second order; first order with respect to urea and to alkyl bromide concentrations.

RECOMMENDATIONS

There appears to be no conflict between the theory of the proposed reaction and the experimental results obtained in this study. However, because of insufficient data and because duplicate runs were not made for purpose of verification, further investigation is required in order to define the mechanism of the reaction with greater confidence.

Experimental Procedure

The procedure used in this study is considered to be generally satisfactory. However, when making runs with 1- bromobutane the use of a water cooled condenser above the test tube instead of an air cooled one may be necessary to prevent the loss of 1- bromobutane through vaporization.

Reaction Mixtures

Kinetic data should be gathered for runs where the alkyl bromide is in excess over the urea, in order to investigate the kinetics of the reaction more thoroughly.

Preparation of reaction mixtures. The solvent, N,N-dimethylformamide, should be heated, preferably below 130°C, and the urea added to the warm solvent, in order to facilitate its solution. The solution should be cooled to room temperature, and then the alkyl bromide may be added. It was observed that the alkyl bromides will react slowly with urea at room temperature, as indicated in Table XX.

Experiments should be planned to use the reaction mixture as soon as possible after formulation in order to avoid introducing indeterminate errors caused by reactions in the mixture at room temperature.

Table XX **Reaction of Alkyl Bromides at Room Temperature**

Reaction Mixture	Alkyl Bromide	Days at Room Temperature	Yield, %
1	C_4H_9Br	77	42.8
2	$C_5H_{11}Br$	20	16.6
3	$C_6H_{13}Br$	20	15.4

REFERENCES

(1) Bradley, J.A., unpublished results, Newark College of Engineering, Newark, N.J., 1963, 1964

(2) Kolthoff, I.M. and Sandell, E.B., Textbook of Quantitative Inorganic Analysis, Third Edition. New York: The Macmillan Company, 1952

(3) Conant, J.B. and Blatt, A.H., The Chemistry of Organic Compounds, Fourth Edition. New York: The Macmillan Company, 1952.