THE KINETICS OF HYDROGEN EXCHANGE

BETWEEN

HYDROXYL GROUPS OF ALCOHOLS

by

BARRY J. NORTH

SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF
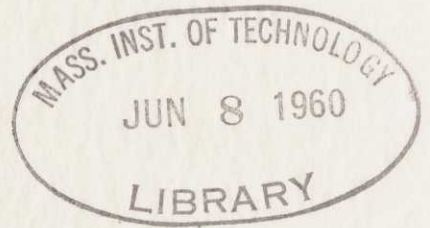
SCIENCE

at the

MASSACHUSETTS INSTITUTE OF

TECHNOLOGY

May,1960

Signature of Author...... *Barry J. North* ......

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DEDICATION

I would like to dedicate this humble work to the memory of my late father for his direction and unimaginable inspiration to me.

ACKNOWLEDGEMENT

I would like to express my appreciation to Dr. C. G. Swain who suggested this problem. For his constructive criticisms during the actual research and particularly during the writing of this thesis I am particularly grateful.

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ABSTRACT

THE KINETICS OF HYDROGEN EXCHANGE
BETWEEN
HYDROXYL GROUPS OF ALCOHOLS

by Barry J. North

Submitted to the Department of Chemistry in partial fulfillment of the requirements for the degree of Bachelor of Science.

The kinetics of tritium-protium exchange between triphenylmethanol and t-butanol was measured in benzene solution at 25° using a flow system. Samples of t-butanol and benzene were collected by "instantaneous" distillation and their specific activities determined using gas-liquid chromatography and liquid scintillation counting. The experimental first-order rate constant for isotope exchange was found to be 0.6 sec.$^{-1}$.

I. INTRODUCTION

The first attempt to study the kinetics of hydrogen exchange between hydroxylic oxygens was made by M. M. Halmann[1]. He investigated the $(C_6H_5)_3COT - (CH_3)_3COH$ system in toluene at 25°. He concluded that exchange was first-order in triphenylmethanol and zero-order in t-butanol. On this basis, plus the fact that exchange was rapid ($k_1 = 0.9 \pm 0.135$ sec.$^{-1}$), he proposed a mechanism for the reaction involving rate-determining rupture of the O--H bond in triphenylmethanol followed by a fast reaction of the resulting ion pair with t-butanol.

Kresge[2] upon reexamination of the problem found Halmann's conclusions invalid. The rate constants calculate from the individual runs varied over the range 0.22 - 6.8 sec.$^{-1}$. Furthermore, the methods used for quenching the reaction and collecting samples introduced gross errors, aside from the main unavoidable error, the unreliability of Halmann's scintillation counter.

In the present investigation the same reaction the same reaction was studied, but the method was modified. To quench the reaction as fast as possible liquid nitrogen cooling was employed. Kresge using a superior scintillation counter and Dry Ice cooling was able to improve the reproducibility of Halmann's method. In the present work, Dry Ice cooling was found to be inadequate and liquid nitrogen was substituted. Furthermore, benzene was used as the solvent because of its superior volatility and quicker solidification upon cooling.

The exchange studied can be represented as:

(1) M. M. Halmann, Laboratory for Nuclear Science Annual Progress Report, May 31, 1955, p.40.
(2) J. Kresge, Report entitled "A Reexamination of the Kinetics of Hydrogen Exchange between Hydroxyl Groups of Alcohols", 1955.

$$(C_6H_5)_3COT + (CH_3)_3COH \rightleftharpoons (C_6H_5)_3COT + (CH_3)_3COT \qquad (1).$$
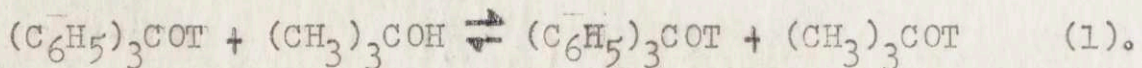
It was followed by the appearance of tritium in the t-butanol. The isotope exchange must be first-order for each set of initial concentrations with respect to the equilibrium point; the experimental first-order foward rate constant, k_e, was determined by plotting the logarithm of the specific activity not exchanged with t-butanol versus time.

II. EXPERIMENTAL

Materials. Triphenylmethanol (100g. Eastman Kodak Co. white label grade) was recrystallized from 400ml. of reagent carbon tetrachloride, m.p. 162-163°, lit.[3] 162.5 . Recrystallized product (50g.) was next dissolved in 300ml. of boiling reagent carbon tetrachloride and allowed to exchange with 0.1 curie of tritiated water (0.1ml.) for 20 min. After recrystallization the tritiated alcohol was dried over phosphorous pentoxide in a drying pistol and stored in an evacuated desiccator over Drierite, yield 42g. t-Butanol (Union Carbide & Carbon, commercial grade) was purified by twice fractionating over Drierite, collecting each time the fraction boiling between 81.5-82.5°. It was stored in a desiccator over Drierite.

An enclosed distillation-buret apparatus was used in preparing and handling the benzene. Benzene (Fisher analytical reagent grade) was refluxed over calcium hydride (Metal Hydrides, Inc., 93-96% pure) for 6-12 hrs. the fractionated and the middle fraction transferred to the buret with a 3-way stopcock (Teflon).

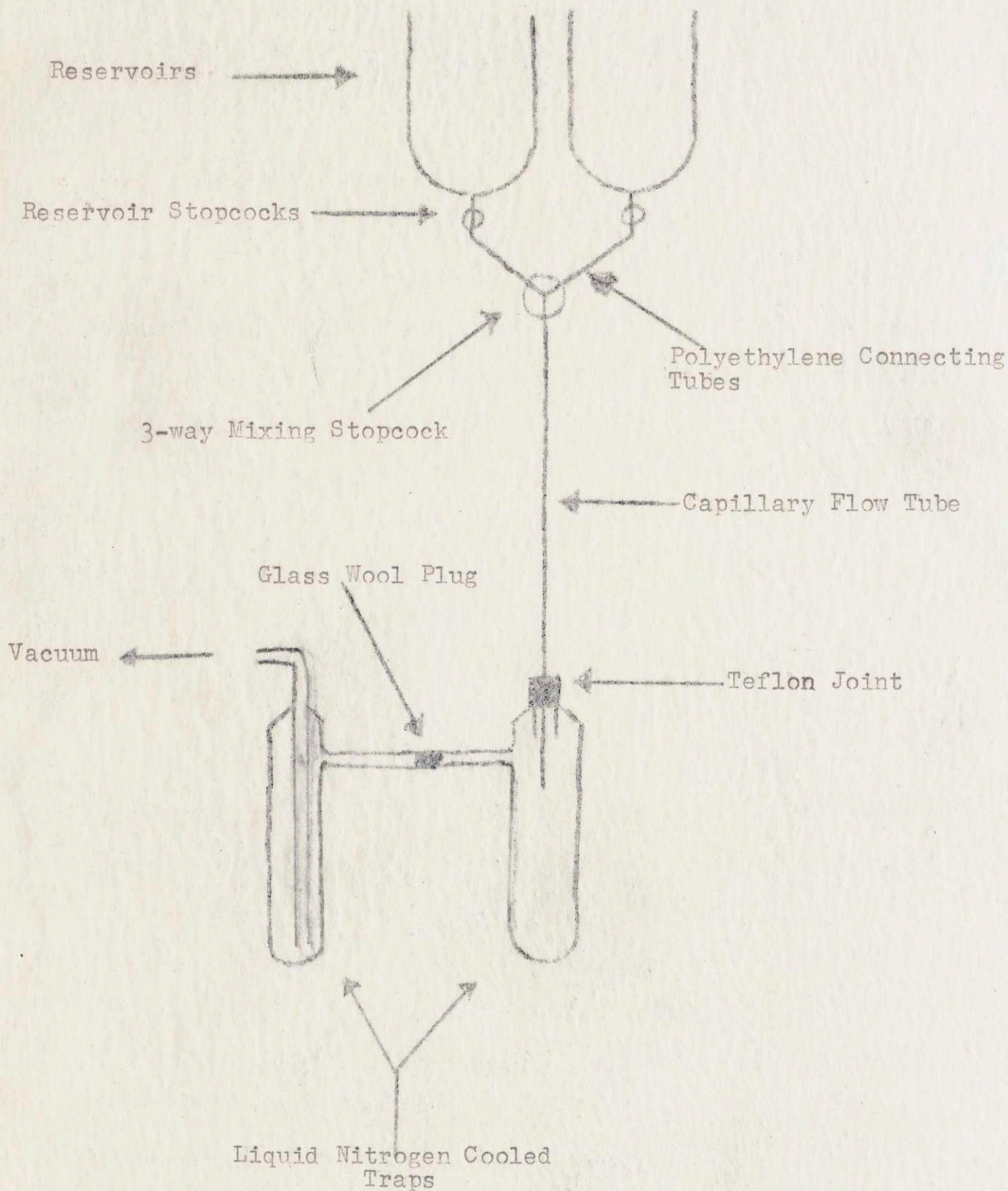(3) A. Bistrzycki, C. Herbst; Ber., 3 5, 3137, 1902.

Kinetic Apparatus. A schematic diagram of the apparatus used is pictured in Fig.1 . All the stopcocks were Teflon, as were the ones in the burets with 3-way stopcocks constructed to dispense stock solutions of the reactants. This avoided the use of stopcock lubricants, which would have contaminated the benzene solutions.

Water-jacketed 125ml. separatory funnels which were detachable from the flow system served as reservoirs. Mixing was accomplished in the 3-way stopcock (originally a Y-stopcock with a V-bore) as the two reactant streams met as a 120° angle. The stream them flowed perpendicularly downward through a passage, having the same internal diameter (1 mm.) as the capillary tube, drilled along the long axis of the stopcock. At the narrow end of the stopcock the stream entered the capillary which was buttjointed inside the stopcock. Then the stream entered the first vacuum trap where most of it was frozen out. Only the small percentage that vaporized before the stream contacted the walls passed on. This was the sample which collected in the second trap. A glass wool plug between the traps prevented entrainment. The ability of the system to mix the reactants and to prevent entrainment was tested using a benzene soluble dye from a red marking pen (Speedry Products, Inc.). With one of the streams dyed, mixing appeared to be completed within the stopcock. Also, no trace of the dye was found in the " sample" collected.

Kinetic Method. Concentrations of the reactants were varied by diluting 0.2 M. stock solutions as desired. Contact time was varied by changing the volume of the capillary and by changing the flow rate through it by use of constrictions.

Fig. 1 . .:SCHEMATIC DIAGRAM OF KINETIC APPARATUS

Reservoirs

Reservoir Stopcocks

Polyethylene Connecting
Tubes

3-way Mixing Stopcock

Capillary Flow Tube

Glass Wool Plug

Vacuum

Teflon Joint

Liquid Nitrogen Cooled
Traps

The contact times were computed by dividing the overall flow times by the volumes that flowed and multiplying this by the capillary volume. To determine the volumes of the capillaries they were filled with mercury and the mercury was poured out and weighed.

Flow rates from the two reservoirs were adjusted to be equal by using needle valves installed in the separatory funnel's stopcocks. Then with the mixing stopcock closed, the system was evacuated and coolant added. A stopwatch was started when the stopcock was opened and stopped when the reservoirs were emptied.

After the sample was collected it was allowed to come to room temperature and then diluted with benzene to approximately 1.5ml. if necessary. One ml. of this was added to 20ml. of scintillator solution which is prepared from 770 ml. reagent toluene (Mallinckrodt Chemical Works), 230 ml. absolute ethanol (Fisher Scientific Co.), 4 g. of 2,5-diphenyloxazole (Arapahoe Chemicals, Inc., scintillation grade), and 15 mg. 1,6-diphenylhexatriene (The Matheson Co., Inc.). The sample was then counted with a Packard automatic Tri-Carb liquid scintillation spectrometer model no. 314-dc the counting error of which is claimed to be about 0.1% and was found reproducible to within no more than one percent by the author.

Analysis. The concentration of t-butanol was determined by gas-liquid chromatography using 0.1 ml. of the sample. An Aerograph chromatographic instrument model no. 2284 manufactured by Wilkins Instrument and Research Inc. coupled with a Honeywell-Brown Electonik recorder model no. Y143X7-VB-II-III-28*N4 with a 10 mv. scale and 2 sec. time constant was

used for the analyses. The column was packed with 15% by weight Dow 710 Silicone on Chromosorb W regular which permitted t-butanol to pass on through before benzene so as not to get lost in the tail of the much larger benzene peak.

Using a uniform sample size of 0.05 ml. the benzene peak was picked up at a sensitivity of 250 and the t-butanol peak at the settings 16,8 and 4. The ratios of the areas determined by cutting out the chart paper representing the areas and weighing them were referred to the sensitivity setting of 16 for the t-butanol peaks. Helium pressure through the column was kept at 3 lbs/ in.^{2} and the column temperature was held at 60°. Two chromatograms were taken for each analysis. The calibration curve of the ratio of the areas under the two peaks (corrected to a standard sensitivity setting for the t-butanol peak) versus concentration appears in Fig. 2.

III. RESULTS AND DISCUSSION

The value obtained for the experimental first-order rate constant of the exchange in benzene with 0.05 M. initial con centrations was 0.595 sec.$^{-1}$. Results are given in Table I and are graphically represented in Fig. 3 .

Not enough runs have been made to justify any conclusions as to reaction orders or mechanism. However, a promising method has been developed ; and while the experimental apparatus used was crude all of the gross sources of error in Halmann's technique were eliminated. Fair reproducibility has been obtained. Furthermore, the rate constant found is considerably lower than that quoted by Halmann as would be expected because he did

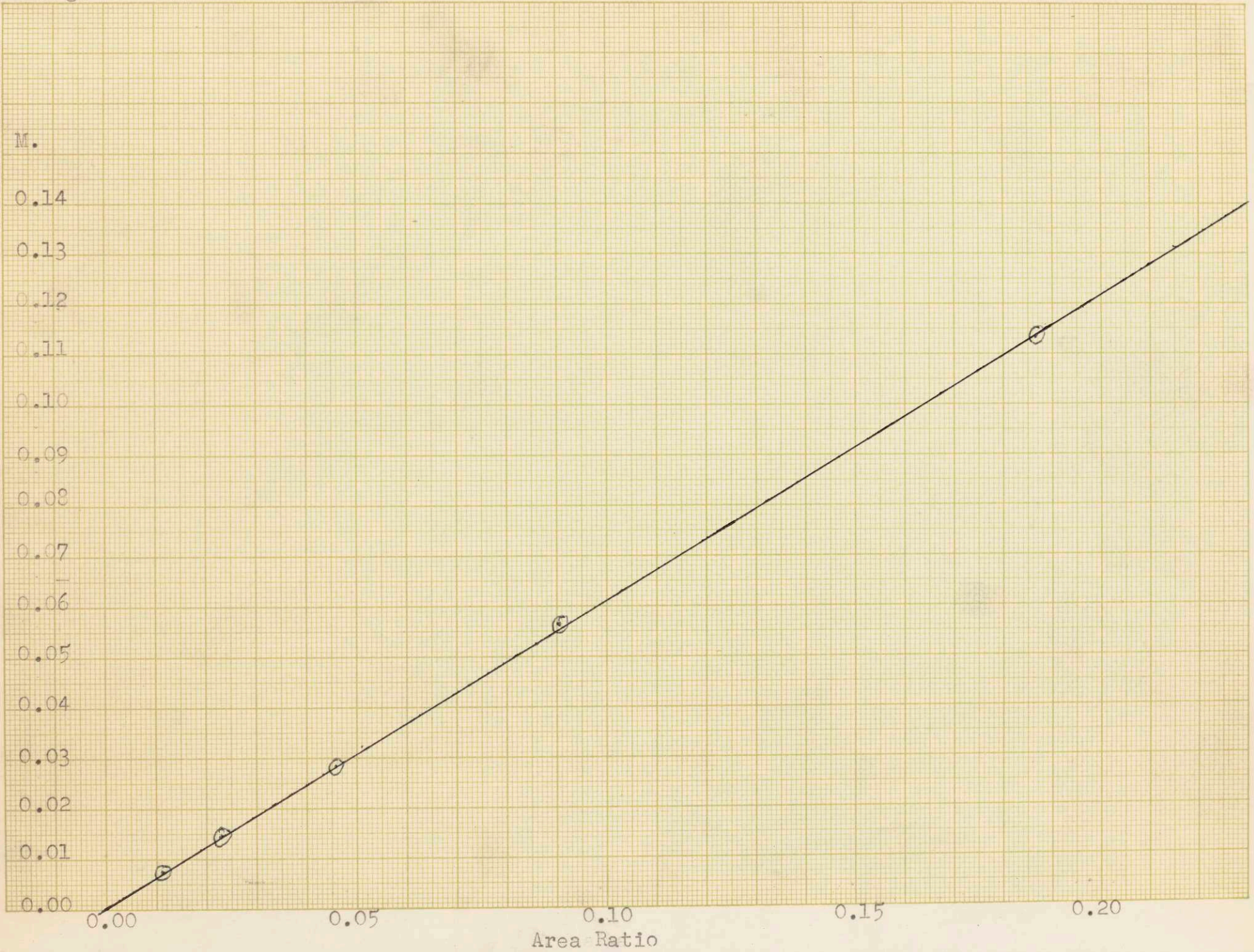Fig. 2 – CHROMATOGRAPHIC CALIBRATION CURVE : AREA RATIO VS. CONC. OF t-BUTANOL IN BENZENE SOLVENT

TABLE I
SUMMARY OF DATA FOR RUNS WITH VARIOUS CONTACT TIMES
TRITIATED TRIPHENYLMETHANOL AND t-BUTANOL, 0.65 M. IN BENZENE AT 25°

Run no.	1	2	3	4	5	
Capillary Volume	0.488	1.10	0.805	0.460	---	ml.
Flow Time	0.596	0.680	1.75	1.075	---	min.
Contact Time	0.005817	0.01496	0.02818	0.00989	∞	min.
Average Activity of Sample over 5min. count	18,207	261,062	196,802	57,387	164,836	counts/min.
Conc. of t-Butanol in Sample	0.1013	0.130	0.042	0.034	0.0202	M.
Specific Activity	0.1797	2.008	4.686	1.688	8.160	counts/min-millimole x 10^{-6}
Infinity Value minus Specific Activity	7.980	6.152	3.474	6.472	0.000	" " " " " " "

In each run 25 ml. of each reactant was used.

FIG. 3 — PLOT OF LOGARITHM OF SPECIFIC ACTIVITY OF UNREACTED t-BUTANOL VS. TIME

-10-

in benzene at 25° 0.05 min.

counts/min.-millimole x 16⁻⁶
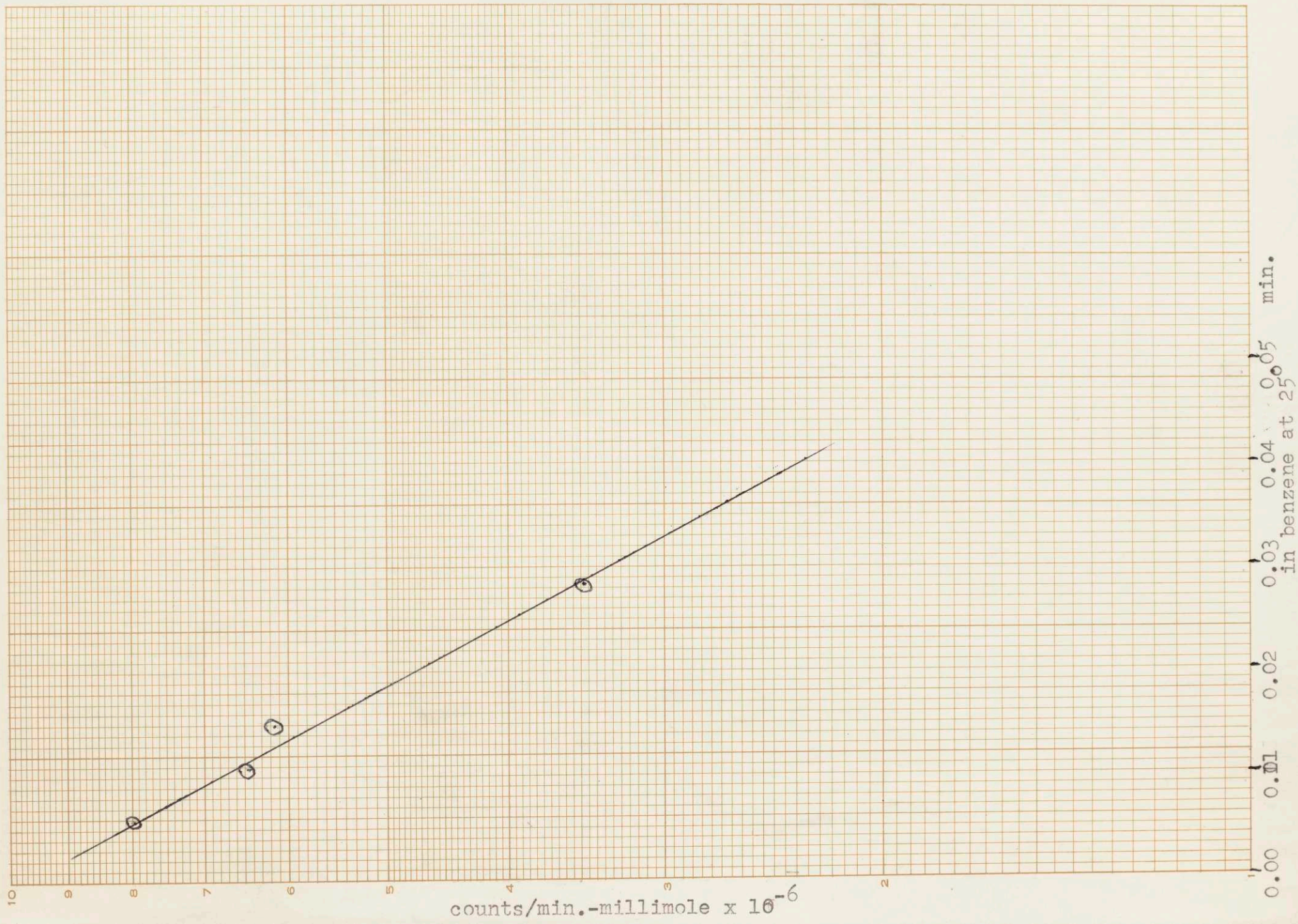
not effectively quench the reaction. The difference in solvent,
used is not sufficient to account for the difference in rates
observed.