Organic and Biological Chemistry

Reactions in Frozen Solutions. III. Methyl Iodide with Triethylamine in Frozen Benzene Solutions

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Abstract: The bimolecular reaction of equimolar methyl iodide and triethylamine in frozen benzene solutions at 3 to −20° follows first-order kinetics, the reactants disappearing with a half-life of 65 min. at −5° independent of initial solution concentrations (0.05 to 0.65 *M*). The reaction has a rate maximum at *ca.* −5°. A soluble "impurity" (*e.g.*, *p*-xylene) present in the frozen benzene solutions depresses the rate and changes the observed kinetics toward the normal second-order kinetics observed in nonfrozen solutions. This reaction in frozen solutions occurs in highly concentrated liquid regions which disappear during a run as soluble reactants are converted to the insoluble product, methyltriethylammonium iodide. The rate of reaction was obtained by measurement of triethylamine and methyl iodide concentrations in thawed samples of a run; the same rate was obtained by measurement (with a single frozen sample) of the decrease in n.m.r. signal from liquid benzene as the benzene crystallized during the reaction. Kinetic equations are derived which correlate the experimental observations.

When a dilute solution containing two reactants is frozen, the reactants may be rejected by the solid phase and become more concentrated in the unfrozen liquid solution. If the reactants are soluble enough, when equilibrium is reached at a temperature above the eutectic temperature of the system there will still exist highly concentrated liquid regions present among the crystalline solvent. In these liquid regions, the reaction between two solutes may be accelerated by the concentration effect. Previous studies[1-4] of reactions in frozen solutions have shown that rates can be sufficiently accelerated so that, although no appreciable reaction occurs in nonfrozen samples at room temperature, prompt reaction occurs in frozen samples at temperatures as much as 50° below room temperature.[5] Other experimentally observed features[1-4] of such frozen solution reactions include reaction rates independent of the method of freezing of kinetic run samples, a maximum rate at an optimum temperature below the freezing point of the solution, variation of kinetic order from that found in the normal (*i.e.*, unfrozen) reaction, and large rate depressions caused by the presence of soluble impurities.

For one case,[1] that of the reaction of *t*-butylperoxy formate with 2,6-lutidine in *p*-xylene, such observations have been shown to be consistent with the following generalized treatment.[6] For a simple bimolecular reaction $A + B \rightarrow$ products, the reaction in a frozen solution occurs in that portion of the system which remains liquid, with a normal reaction rate equal to $k_2A_hB_h$. This rate is in terms of moles per second per *liter of reaction volume.* To obtain the observed rate (in terms of moles per second per *liter of thawed solution*) it is necessary to multiply by the ratio V_h/V_s which decreases the rate in the reaction volumes of frozen samples to that measured in thawed samples. The observed rate of reaction is then given by eq. 1.[7]

$$\frac{dA_s}{dt} = -k_2A_hB_h\frac{V_h}{V_s} \qquad (1)$$

As previously indicated,[1] the reaction volume V_h may increase or decrease during a kinetic run as the number of moles which must be accommodated in the liquid regions at constant concentration increase or decrease. However, in the reaction of *t*-butylperoxy formate with 2,6-lutidine in *p*-xylene, the reaction volume was constant throughout a run as 1 mole of reactant was replaced by the equivalent of 1 mole of soluble product. To investigate the consequences of the variation of reaction volume during a run, we have studied the reaction of methyl iodide with triethylamine in frozen benzene solutions. Here the product, methyltriethylammonium iodide, is insoluble in benzene, and it is expected that the reaction regions will disappear during a run as soluble reactants are converted to insoluble product.

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(1) R. E. Pincock and T. E. Kiovsky, *J. Am. Chem. Soc.*, **87**, 2072 (1965); **87**, 4100 (1965).

(2) (a) A. R. Butler and T. C. Bruice, *ibid.*, **86**, 313 (1964); (b) *ibid.*, **86**, 4104 (1964).

(3) N. H. Grant, D. E. Clark, and H. E. Alburn, *ibid.*, **83**, 4476 (1961).

(4) W. H. Prusoff, *Biochim. Biophys. Acta*, **68**, 302 (1963).

(5) Accelerative effects other than the "concentration effect" also may be operative in some frozen solution reactions.[2-4] See also H. E. Alburn and N. H. Grant, *J. Am. Chem. Soc.*, **87**, 4174 (1965).

(6) The notation used is as follows: A_h, B_h and A_s, B_s are the concentrations of the reactants in the liquid regions of a frozen solution and in the thawed solution, respectively. V_h is the total volume of the liquid regions in a frozen solution, V_s is the volume of the thawed solution, C_h is the total constant concentration of solutes in the liquid regions of a frozen solution, k_2 is the normal second-order rate constant for bimolecular reaction, and Im_s is the solution concentration of any inert solutes.

(7) If the reaction components are present only in the liquid part of a frozen solution then $A_sV_s = A_hV_h$, $B_sV_s = B_hV_h$, and substitution in eq. 1 gives $dA_s/dt = -k_2A_sB_sV_s/V_h$. Since the normal reaction rate in an unfrozen solution is $k_2A_sB_s$ the acceleration in frozen solutions is given by the ratio of volume of solution to the total volume of liquid regions in the frozen solution, *i.e.*, V_s/V_h. For the reaction of *t*-butylperoxy formate with 2,6-lutidine in *p*-xylene at 0° the maximum observed relative increase in rate was 400.[1]

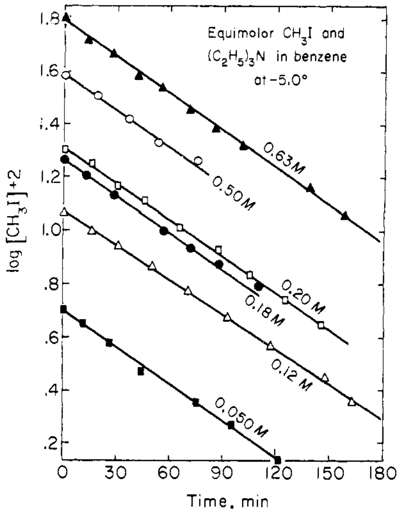

Figure 1. First-order plots for reaction of equimolar concentrations of methyl iodide with triethylamine in frozen benzene solutions at −5°.

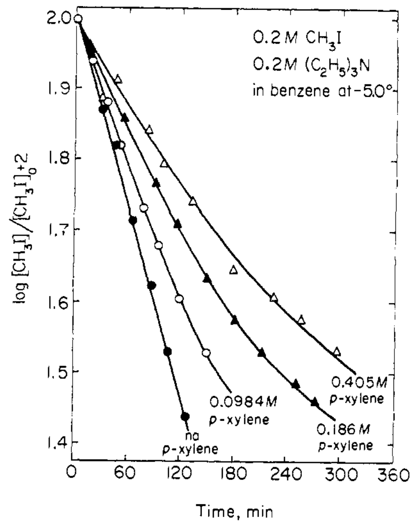

Figure 2. First-order plots for reaction at −5° of 0.2 *M* methyl iodide with 0.2 *M* triethylamine in frozen benzene solutions containing various concentrations of *p*-xylene.

Results

The rate of reaction of methyl iodide with triethylamine in frozen benzene solutions was studied by measurement, after thawing the samples of a run, of the loss of methyl iodide infrared absorption at 1240 cm.$^{-1}$, and by measurement of the triethylamine concentration by titrimetric analysis. The reaction rate was also obtained, utilizing a single frozen sample, by n.m.r. spectroscopy. For runs using the former two methods, individual kinetic samples in small ampoules were made up by combining measured volumes of solutions of the reactants in benzene. As the reaction at room temperature is rather fast, the ampoules were sealed quickly and frozen in Dry Ice–acetone. After similar preparation of all the samples, they were brought to the temperature of the run, withdrawn periodically, thawed, and analyzed. Freezing of samples in different ways[1] (*e.g.*, in liquid nitrogen) had no effect on the observed rate.

Methyl iodide reacts with triethylamine in unfrozen benzene solutions according to simple second-order kinetics.[8] However, with equal concentrations of reactants in frozen benzene solutions plots of reciprocal concentration against time were always distinctly curved, and it became apparent that only plots of log (concentration) against time gave good straight lines for more than 2 half-lives. The frozen solution reaction with equal concentrations of reactants is then a first-order reaction. Figure 1 shows runs for equal concentrations of methyl iodide and triethylamine from 0.05 to 0.63 *M* in frozen benzene at −5°. The first-order rate constants (see Table I) over this range of initial solution concentration are all essentially the same, half-lives varying only from 62 to 72 min.

From the activation parameters reported[9] for second-order reaction of methyl iodide with triethylamine in liquid benzene solutions the rate at −5° is calculated to be 2.4×10^{-4} l. mole^{-1} sec.$^{-1}$. For a 0.05 *M* initial concentration of both reactants the half-life is then 1400 min. and the observed half-life of 65 min. shows the moderate acceleration which occurs on freezing.[7] With more dilute initial solutions the relative rate increase on freezing would be greater.

Table I. Rate Constants for Reaction of Equimolar Triethylamine with Methyl Iodide in Frozen Benzene Solutions at −5.0°

MeI concn., *M*	Et_3N concn., *M*	Method	$k_2C_h \times 10^4$ sec.$^{-1}$
0.206	0.196	Infrared	3.24[a]
0.118	0.117	Infrared	3.22
0.200	0.200	Infrared	3.35
0.199	0.206	Titra.	3.40
0.050	0.050	Infrared	3.56
0.474	0.500	Titra.	3.55
0.636	0.616	N.m.r.	3.49
	With Added *p*-Xylene[b]		
0.217	0.212	0.0984[c]	3.64[d]
0.198	0.209	0.186[c]	3.35[d]
0.204	0.204	0.405[c]	3.66[d]
0.146	0.146	0.251[c]	2.92[e]

[a] Calculated from first-order plots, $k_{obsd} = k_2C_h/2$. [b] Rate constants calculated by use of eq. 2. [c] Concentration of *p*-xylene, *M*. [d] Titration method of analysis used. [e] Infrared method of analysis used.

Addition of *p*-xylene to runs having equal reactant concentrations causes deviations from the linear log (concentration) *vs.* time relationship. Figure 2 shows first-order plots for runs at −5° containing various concentrations of *p*-xylene. With greater concentrations of this soluble "impurity" the rate of loss of methyl iodide and triethylamine is decreased, and the deviation from the first-order kinetics found in the absence of *p*-xylene becomes more evident. At the highest concentration of *p*-xylene used, 0.405 *M*, a plot of the data according to second-order kinetics (*i.e.*, reciprocal concentration against time) gave a slightly S-shaped curve, but with a great deal more similarity to a straight line than found in a first-order plot.

The results for rate studies with equimolar reactant concentrations at various temperatures (see Table II)

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(8) (a) N. Menschutkin, *Z. physik. Chem.*, 5, 589 (1890); (b) see also C. G. Swain and R. W. Eddy, *J. Am. Chem. Soc.*, 70, 2989 (1948); Y. Pocker, *J. Chem. Soc.*, 1279 (1957).

(9) H. C. Raine and C. N. Hinshelwood, *ibid.*, 1378 (1939).

Table II. Rate Constants[a] for Reaction of Equimolar Triethylamine with Methyl Iodide in Frozen Benzene Solutions at Various Temperatures

MeI concn., M	Et_3N concn., M	Temp., °C.	$k_2C_h \times 10^4$ sec.$^{-1}$
0.182	0.197	2.5	1.97[a,b]
0.206	0.200	0.0	2.92
0.206	0.200	−1.5	2.89
0.198	0.199	−3.0	3.26
0.200	0.200	−5.0	3.35
0.199	0.206	−5.0	3.40[b]
0.200	0.200	−7.0	3.30
0.200	0.200	−9.3	3.10
0.200	0.200	−15.3	2.52
0.182	0.197	−20.0	1.85[b]

[a] Calculated from first-order plots, $k_{obsd} = k_2C_h/2$. [b] Titration method of analysis used, all others by infrared analysis.

Table III. Rate Constants for Reaction of Unequal Concentrations of Triethylamine with Methyl Iodide in Frozen Benzene Solutions at −5.0°

MeI concn., M	Et_3N concn., M	MeI,[a] %	$k_2C_h \times 10^4$ sec.$^{-1}$
0.125	0.378	31	3.18[b]
0.152	0.300	34	3.10
0.146	0.211	41	3.12
0.200	0.158	56	3.87
0.344	0.186	65	4.48
0.311	0.145	68	4.34
0.364	0.127	74	4.26

[a] Percentage of solute at the start of the reaction which is methyl iodide. [b] Rate constants were calculated by use of eq. 3.

and for unequal concentrations at −5° (Table III) are described more fully below. The results may be summarized by stating that the reaction in frozen solutions shows a maximum rate at *ca.* −5° and also occurs at convieniently measurable rates at +3 and at −20°. For runs at −5° with unequal concentrations of reactants, treatment of the data according to an equation developed in the Discussion gave rate constants consistent with those found for runs at equal concentrations.

Discussion

As outlined in the Introduction, the kinetic treatment of frozen solution reactions is based on the presence of liquid regions containing high and constant concentrations of reactants. It is the high concentration[10] which gives rise to the observed rate accelerations and the requirement of constant total concentration which leads to the rather unusual changes in kinetic order and sensitivity to soluble impurities. In order to keep a constant concentration, the walls of the liquid regions may thaw or freeze to accommodate more or less solute. In the case of the reaction of triethylamine with methyl iodide, the formation of an insoluble product[11] results in a decrease of the reaction volume during a run. As methyltriethylammonium iodide is formed, it is precipitated out and the walls of the reaction regions close in to hold the concentration of the remaining solute at a constant value. The observed first-order kinetics for this bimolecular reaction is a consequence of this volume change; the concentrations A_h and B_h are constant, and according to eq. 1 the rate is then proportional to the reaction volume V_h. Since this volume in a frozen solution is proportional to the total concentration in a thawed solution (*i.e.*, $V_h = (A_s + B_s)V_s/C_h$), the reaction rate is proportional to the sum of reactant concentrations (leading to first-order kinetics for equal reactant concentrations) rather than the product of their concentrations (*i.e.*, second-order kinetics).

To obtain the integrated rate expression for reaction at equal reactant concentrations, with the added complication of the presence of a soluble "impurity" (*Im*), the assumption is made that all solutes present in an unfrozen solution are present in the liquid regions of the frozen solution, *i.e.*, $A_sV_s = A_hV_h$, $B_sV_s = B_hV_h$ and $(A_s + B_s + Im_s)V_s = C_hV_h$. Substitution into eq. 1 and integration then gives eq. 2. This equation is a combination of the form of the kinetic equations for first-order reaction (ln A_s) and for second-order reaction at equal reactant concentrations ($1/A_s$).

$$2\ln(A_s) - \frac{Im_s}{A_s} = -k_2C_ht + \text{constant} \qquad (2)$$

When no inert solutes are present, $Im_s = 0$, and a plot of log A_s against time should be a straight line with slope $k_2C_h/2 \times 2.3$. Figure 1 shows that this relationship is experimentally obtained, and that, as required by eq. 2, the slopes of the plots for runs with different initial solution concentrations are very nearly the same (see also Table I). In this reaction, unlike the base-catalyzed decomposition of *t*-butylperoxy formate in frozen solution,[1] the observed first-order rate constant, $k_{obsd} = k_2C_h/2$, is independent of the reaction volume during a run and therefore independent of the initial solution concentration which determines this initial reaction volume in a frozen solution.

When an inert solute such as *p*-xylene is present, the "second-order" portion of eq. 2 comes into play. Plots of the data according to simple first-order kinetics (see Figure 2) show the deviation caused by the neglect of this "second-order" term, which becomes more important at high "impurity" concentration or when the reaction is more complete. The reaction slows down because the reaction volumes no longer continue to decrease in proportion to the reactant concentrations. At low reactant concentrations the reaction regions are held open by the "inert" solute, the reactants then become continuously more dilute, and the reaction kinetics transform into the ordinary second-order kinetics which would be observed at constant volume. The fact, as indicated in the Results section, that a plot of reciprocal A_s against time for a run with high *p*-xylene concentration is a good approximation to a straight line is an outcome of this effect.

Treatment of the data for runs containing *p*-xylene according to the complete form of eq. 2 is shown in Figure 3. This equation corrects, during a run, for the continuous decrease in rate of contraction of the total reaction volume. The slopes of these corrected plots should be equal to $k_2C_h/2.3$. Table I contains the data for runs at equal concentration, with and without added *p*-xylene. The values of k_2C_h obtained in both

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[10] From freezing point–composition data for methyl iodide or triethylamine in benzene the concentration of the liquid regions at −5° is 1.6 *M*.

[11] No freezing point depression was observed for benzene saturated with methyltriethylammonium iodide.

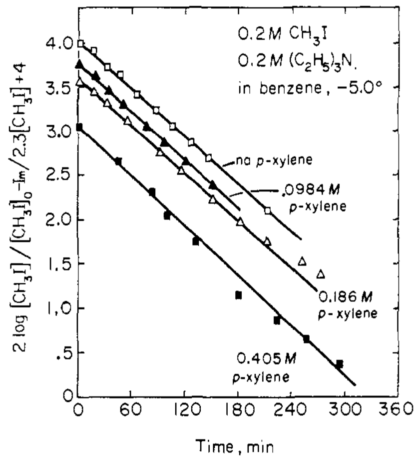

Figure 3. Corrected first-order plots (according to eq. 2) for reaction at −5° of 0.2 *M* methyl iodide with 0.2 *M* triethylamine in frozen benzene solutions containing *p*-xylene.

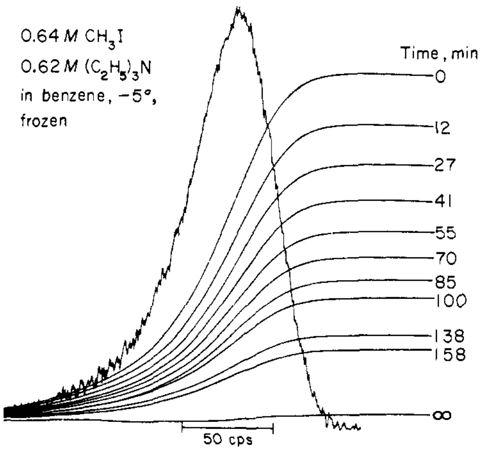

Figure 5. N.m.r. signal (and integral curves at various times) arising from liquid benzene present at −5° in a frozen benzene solution initially containing 0.64 *M* methyl iodide and 0.62 *M* triethylamine.

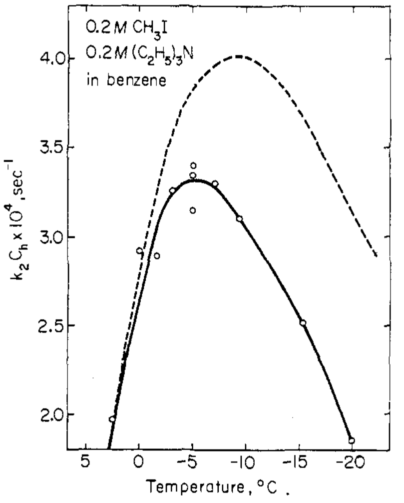

Figure 4. Dependency of observed first-order rate constants ($k_{\text{obsd}} = k_2C_h/2$) on temperature for the reaction of equimolar concentrations of methyl iodide with triethylamine in frozen benzene solutions: – – –, calculated k_2C_h; ———, observed k_2C_h.

cases are essentially the same and indicate the success of eq. 2.

Frozen kinetic runs in solutions initially containing widely differing concentrations of reactants would be expected to give data somewhat analogous to that from runs with equal reactant concentration but with an inert solute present. In other words, the excess of one reactant (acting like an inert impurity) would tend to keep the reaction volume from decreasing at a constant rate as the reaction proceeds. Accordingly, when data from runs at different initial reactant concentrations were treated by the normal equation for second-order reactions, the plots of log A_s/B_s against time were good straight lines. However, integration of eq. 1 for the case of unequal reactant concentrations and no inert solute gives rise to eq. 3, which is more directly

$$\ln(A_sB_s) = -k_2C_ht + \text{constant} \qquad (3)$$

applicable to this type of bimolecular reaction in frozen solutions. Plots of log (A_sB_s) against time for runs at unequal concentration were good straight lines. The values of k_2C_h obtained from the slopes of these lines are given in Table II. It may be seen that these values[12] are consistent with the same quantity obtained from eq. 2 for runs at equal concentrations, with or without "impurity".

The temperature dependence of the observed rate constants at equal reactant concentration, $k_{\text{obsd}} = k_2C_h/2$, arises from a decrease in k_2 and an increase in C_h as the temperature is lowered. The change in k_2 may be calculated from the available activation parameters,[9] while C_h is obtained from the experimental relation of concentration of solute to freezing point of benzene solutions.[14] Figure 4 shows the experimentally observed values of k_2C_h (solid line) for runs from 2.5 to −20° compared to calculated values (broken line). At −5° the theoretical value of k_2C_h differs from the experimental value by about 13%.

Finally, the variation of the volume of reaction regions during a kinetic run and the previous use of n.m.r. spectrometry to indicate relative changes in the composition of the liquid phase present in frozen solutions[1] suggested that the rate of reaction of triethylamine with methyl iodide might be directly measured in a single frozen sample by a method based on n.m.r. The p.m.r. spectrum[15] at −5° of a solution of 0.64 *M* methyl iodide and 0.62 *M* triethylamine in benzene (the sample initially frozen at −70°) showed a broad peak near the region of absorption of liquid benzene (τ 2.63). This peak, which is due to the benzene present in the liquid reaction regions of the frozen sample, slowly decreased in intensity. Figure 5 shows the form of the initial spectrum and of the integral curves taken at various times. These integral values are proportional to the number of moles of liquid benzene

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[12] The slight increase in observed rate constant for runs with relatively high concentration of methyl iodide (see Table III) may be due to a solvent effect. The reaction regions at −5° contain 1.6 *M* (*ca.* 12 mole %) solute; if this is predominantly methyl iodide (dielectric constant 7.00) rather than triethylamine (dielectric constant 2.42) an increase in rate might occur.[8b] The great sensitivity of alkyl halide–amine reactions to solvent variation is well established.[13]

[13] N. Menschutkin, *Z. physik. Chem.*, 6, 41 (1890).

[14] The same molar concentration of methyl iodide or triethylamine in benzene depresses the freezing point to the same extent down to *ca.* −10° (2.4 *M*), but divergence of the freezing point–concentration relationships for the two solutes occurs below −10°.

[15] Nuclear magnetic resonance spectra were obtained using a Varian A-60 spectrometer.

in that small portion of the frozen sample which gives rise to the signal. As the liquid reaction regions are filled predominantly with benzene the integral values are also approximately proportional to the volume, V_h, of the liquid regions of the frozen sample. The relationship of the changes in integral value, reaction volume of frozen solutions, and concentration of thawed solutions follows from the assumptions that all the solutes are present in the reaction volumes (*i.e.*, $C_hV_h = 2A_sV_s$ for equal reactant concentrations), that the concentrations in the reaction regions are constant, and that the integral value is proportional to the volume of the liquid regions of a frozen solution. The result is that the change in one is related to the change in another by $\mathrm{d} \ln (\text{integral value})/\mathrm{d}t = \mathrm{d} \ln V_h/\mathrm{d}t = \mathrm{d} \ln A_s/\mathrm{d}t = -k_{\mathrm{obsd}} = -k_2C_h/2$. A plot of log (integral value in millimeters) against time is a straight line and the rate constant, $k_{\mathrm{obsd}} = k_2C_h/2$, obtained from the slope of this line gave k_2C_h as 3.5×10^{-4} sec.$^{-1}$. This is the same as the average value 3.4×10^{-4} sec.$^{-1}$ obtained by analysis of thawed samples using infrared and titration techniques (see Table I). The rate of reaction (obtained from the reactant concentrations in thawed samples of a run) and the rate of change of the reaction volume (obtained by measurement of the loss of n.m.r. signal arising from the liquid solvent) in frozen benzene solutions are thus shown to be experimentally related. Both the change of concentration, $\mathrm{d} A_s/\mathrm{d}t = -k_{\mathrm{obsd}}A_s$, and the change of reaction volume, $\mathrm{d} V_h/\mathrm{d}t = -k_{\mathrm{obsd}}V_h$, are first-order processes. The observed rate constants under the condition of equal reactant concentrations are experimentally identical, as expected if loss of reactants results in a corresponding contraction of the reaction volume.[16]

Experimental Section

Materials. Methyl iodide (Eastman Organic Chemicals, reagent grade) was washed with dilute aqueous sodium thiosulfate solution and with water. After drying over anhydrous calcium chloride and distillation (b.p. 44° (752 mm.)) through a column packed with glass beads, the product was stored in a brown bottle over a drop of mercury. Reagent grade triethylamine was refluxed over and distilled (b.p. 89°) from barium oxide. *p*-Xylene used was as previously described.[1]

Reagent grade benzene was recrystallized three times by slow freezing of *ca.* 75–85% of the total volume. Benzene which had been dried over anhydrous magnesium sulfate, distilled, then crystallized once, gave the same rate for reaction of methyl iodide with triethylamine. Benzene used had freezing point of 5.6°.

Kinetic Methods. A. Infrared Method. Solutions of equal (or nearly equal) concentrations of methyl iodide and of triethylamine were prepared, equal volumes of these were combined, and the resulting solution was shaken vigorously to mix thoroughly the reactants. This mixture (some product immediately begins to precipitate) was drawn quickly into a large syringe and divided into a number of samples held in 1-ml. vials. The vials were sealed and plunged into a Dry Ice–acetone or liquid nitrogen bath. When the solutions in the vials were frozen, the vials were all transferred to a constant temperature bath at the desired temperature. After allowing the samples to warm up to the bath temperature, the first vial (time zero) was removed and placed in a Dry Ice–acetone bath. After all the samples of a run had been collected in this manner, they were thawed and analyzed by measuring the change in absorbance at 1240 cm.$^{-1}$ due to methyl iodide. Both benzene and triethylamine absorb relatively weakly in this region. However benzene was compensated for by pure solvent in the reference cell. The sodium chloride cells used had path lengths of 0.5 mm. The observed rate constant, for reactions with equal reactant concentrations, were obtained by plotting log $((A_0 - A_\infty)/(A_t - A_\infty))$ against time in minutes and multiplying the slope of this line by 2.303/60. A_0, A_t, and A_∞ are the values of sample absorbance, measured against pure benzene in the reference cell, at time zero, time t, and time infinity (usually 10 half-lives), respectively. In all cases in which the absorbance of an infinity sample was measured it was found to be zero.

B. Titration Method. Solutions of the reactants having twice the desired concentration of the run were made up, then 2- or 3-ml. portions of one solution were pipetted into a number of *ca.* 6-ml. vials. An equal amount of the second solution was pipetted into the first vial which was then immediately shaken, sealed, and frozen in a Dry Ice–acetone or liquid nitrogen bath. After all the vials had been prepared in this manner they were placed in the constant temperature bath. The first sample was withdrawn about 10 min. later when temperature equilibration was complete. The samples were thawed immediately after withdrawing from the bath by shaking under warm tap water. The solution was washed into excess standard hydrochloric acid (0.1 *N*) and the excess acid was back titrated to the methyl red end point with standard 0.1 *N* sodium hydroxide solution. Some little scatter in the points of a run seemed due to the use of individually prepared samples, rather than aliquots of a single solution. For runs with unequal reactant concentrations (A_s and B_s) the observed rate constants were obtained by plotting log (A_sB_s) against time in minutes and multiplying the slope of the line by 2.303/60. When *p*-xylene was added as an "impurity" it was added to the original triethylamine solution so that its concentration was twice as great as in the final reaction mixture. For runs with *p*-xylene present the rate constants were obtained from a plot of $2 \log (A_s/A_0) - Im_s/2.303A_s$ against time. The slopes of these plots are equal to $k_2C_h/2.303$.

C. Nuclear Magnetic Resonance Method. A solution 0.6 *M* in both methyl iodide and triethylamine in benzene was prepared and about 1 ml. was transferred quickly with a syringe to a normal n.m.r. sample tube. The sample was frozen in Dry Ice–acetone and then placed in a Varian A-60 n.m.r. spectrometer equipped with variable-temperature control. The temperature of −5° was measured by the separation of the peaks of a methanol sample. After the sample came up to −5° the integral curve for the broad benzene peak was run about every 15 min.[17] An infinity sample, prepared as given above for the single sample used in the run, had been held at −5° overnight and gave an integral curve only 2% as high as that given by the initial zero time integral curve. A plot of log (integral value in millimeter) against time was a good straight line over 80% reaction; the slope of the line multiplied by 2 × 2.303 gave the value of k_2C_b as 3.5×10^{-4} sec.$^{-1}$.

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(16) A disadvantage of this n.m.r. kinetic method is the necessity to use solutions with high initial concentrations. The total concentration of 1.26 *M* allows, at the start of the reaction, only about 20% of the solvent to be crystallized, while 0.1 *M* runs analyzed by infrared techniques were 94% solid at the start of the run.

(17) The peak width at half-height was *ca.* 50 c.p.s., much narrower than signals arising from crystalline solids.