214. *Kinetics of the Reaction between Methyl Iodide and Trimethylamine in Carbon Tetrachloride Solution.*

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The kinetics of the reaction between methyl iodide and trimethylamine in carbon tetrachloride have been studied experimentally in the absence of the vapour phase. Static measurements have also been made. Solutions of the halide are regular, with an interchange energy of 215 ± 7 cal./mole. Solutions of the amine are highly irregular: the activity coefficient of the solute decreases rapidly with increase in concentration in regions of kinetic interest. Tetramethylammonium iodide is insoluble in carbon tetrachloride but dissolves in the presence of either methyl iodide or trimethylamine. Crystals of the product are deposited during early stages of the reaction, and the reaction is complicated by the attainment of a heterogeneous equilibrium. In solutions containing excess of methyl iodide, the second-order velocity constant increases, and in solutions containing excess of trimethylamine it decreases as reaction proceeds. The data obtained on the kinetics of the reaction in the homogeneous phase are not inconsistent with a kinetic order of 2 and with an intrinsically low velocity coefficient.

THE rate at which amines and organic halides react in solution has been the subject of numerous experimental studies since the appearance of Menschutkin's paper.[1] There have also appeared many discussions of their molecular statistics. These reactions are predominantly of the second kinetic order, though departures from a normal behaviour have been noted, particularly in solvents consisting of molecules which in the gas phase have no permanent dipole moments. Grimm, Ruf, and Wolff,[2] for example, found a drift in the second-order constants governing the reaction between ethyl iodide and trimethylamine in benzene and in *p*-dichlorobenzene. Moelwyn-Hughes and Hinshelwood[3] simultaneously and independently recorded a similar anomaly for the same reaction in carbon tetrachloride. The experimental technique employed in these and in all subsequent investigations differs little from that used by Menschutkin. The present paper records some experiments on the reaction $MeI + NMe_3 \longrightarrow NMe_4I$ in carbon tetrachloride solution carried out in the absence of the vapour phase. Its object was to extend such experimental knowledge as we now possess on the rates of chemical reactions between polar molecules in inert solvents.

EXPERIMENTAL

Purification of Reagents.—Methyl iodide was shaken with pellets of potassium hydroxide, washed with water, dried (Na_2SO_4), distilled from phosphoric oxide, and stored in the dark over mercury. From its vapour pressure, which was measured at 20 temperatures between 252·70° and 330·86° K, its boiling point was found to be 315·61° K, which is intermediate between the value of 315·55° given by Brown and Acree[4] and that of 315·66° given by Timmermans.[5]

The starting specimen of trimethylamine contained traces of mono- and di-methylamine, methanol, and moisture. 15-ml. samples were vaporised in a vacuum-system and cycled 3 times through bubblers containing acetic anhydride, which removed the contaminating amines, methanol, and most of the water. Two distillations at room temperatures removed most of the acetic anhydride. The next purification was by distillation at the temperature of solid carbon dioxide, passage over calcium oxide, and condensation in a trap cooled by liquid nitrogen. The liquid amine was kept over potassium for two days and finally distilled. The pure sample gave a vapour pressure[6] of 681 ± 1·0 mm. at 0°. Apiezon M grease was found to be a suitable tap

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[1] Menschutkin, *Z. phys. Chem.*, 1890, **5**, 589.
[2] Grimm, Ruf, and Wolff, *ibid.*, 1931, **13**, *B*, 301.
[3] Moelwyn-Hughes and Hinshelwood, *J.*, 1932, 230.
[4] Brown and Acree, *J. Amer. Chem. Soc.*, 1916, **38**, 2145.
[5] Timmermans, " Physicochemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950.
[6] Swift and Hochanadel, *J. Amer. Chem. Soc.*, 1945, **67**, 880.

lubricant. Trimethylamine was estimated by titration with standard nitric acid, bromocresol-green being the indicator.

Carbon tetrachloride was washed twice with 2N-sodium hydroxide, with dilute hydrochloric acid, and finally with water. After being dried overnight over calcium oxide, and distilled from phosphoric oxide, it gave a satisfactory vapour pressure and refractive index.

Solutions of Methyl Iodide in Carbon Tetrachloride.—The equilibrium between the liquid and vapour phases of mixtures of methyl iodide and carbon tetrachloride was investigated by a standard procedure, the composition of either phase being determined refractometrically. Pressures, read on a calibrated manometer, are recorded in mm. of Hg reduced to 20°. At each temperature the relation between the total pressure, P, of the system and its compositions expressed in molar fractions, x, was examined in the light of the equation

$$P = p_1{}^\circ x_1 \exp(x_2{}^2\alpha) + p_2{}^\circ x_2 \exp(x_1{}^2\alpha) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $p_1{}^\circ$ and $p_2{}^\circ$ are the vapour pressures of pure carbon tetrachloride and methyl iodide respectively, and

$$\alpha = \Delta U^\circ/\boldsymbol{R}T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where ΔU° is the interchange energy. Equation (1) was obeyed over all the conditions examined, so that the systems may be regarded as regular solutions in the sense applied by Hildebrand. In terms of the pressure, P, exerted by those systems which contain equimolar liquid mixtures, we have from equation (1),

$$\alpha = \Delta U^\circ/\boldsymbol{R}T = 4 \ln [2P/(p_1{}^\circ + p_2{}^\circ)] \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The experimental results summarised in Table 1 show that ΔU° is constant to within ±7 cal. in the temperature range examined. Later and more precise work since completed in this laboratory by Mr. R. W. Missen shows that $\Delta U^\circ = 203 \pm 2$ cal. The present data yield activity coefficients of sufficient accuracy for our needs. For systems which obey equation (1), the molar chemical potential of methyl iodide is

TABLE 1. *Interchange energy in the methyl iodide–carbon tetrachloride system.*

T (°K)	$p_1{}^\circ$ (mm. Hg)	$p_2{}^\circ$ (mm. Hg)	$P(x = \frac{1}{2})$	α	ΔU° (cal./mole)
283·19	55·65	219·7	152	0·396	223
303·15	139·6	492·8	345	0·348	210
313·17	210·9	699·9	495	0·334	208
323·32	309·0	966·4	694	0·339	218
333·36	443·0	1298	944	0·326	216
				Average =	215 ± 7

$$G_2 = G_2{}^{\mathrm{L}} + \boldsymbol{R}T \ln x_2 + \Delta U^\circ(1 - x_2)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $G_2{}^{\mathrm{L}}$ is the molar free energy of the pure liquid. To obtain activity coefficients in the dilute regions which are of kinetic interest, we may also write

$$G_2 = G_2{}^\circ + \boldsymbol{R}T \ln c_2 + \boldsymbol{R}T \ln \gamma_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $G_2{}^\circ$ is the molar chemical potential in an ideal solution of unit concentration (1 mole per l. of solution), and γ is the activity coefficient on this concentration basis. In dilute solutions, $x_2 = c_2V_1{}^\circ/1000$, where $V_1{}^\circ$ is the molar volume of the solvent. Hence, approximately,

$$G_2{}^\circ = G_2{}^{\mathrm{L}} + \Delta U^\circ + \boldsymbol{R}T \ln (V_1{}^\circ/1000)$$

and

$$\ln \gamma_2 = -\frac{\Delta U^\circ}{\boldsymbol{R}T} \cdot \frac{V_1{}^\circ}{500} c_2 + \frac{\Delta U^\circ}{\boldsymbol{R}T}\left(\frac{V_1{}^\circ}{1000}\right)^2 c_2{}^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

At 298·16° K, $V_1{}^\circ$ is 97·10 c.c./mole. Hence

$$\log_{10} \gamma_2 = -0{\cdot}0306c + 0{\cdot}00149c^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

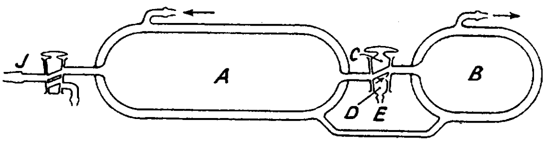
Activity coefficients of methyl iodide in dilute solutions in carbon tetrachloride derived from this equation are given in Table 2. Kinetic experiments have been confined to solutions containing initially not more than 400 mmoles of methyl iodide per l. of solution. Within this range, therefore, the solutions deviate from van't Hoff's laws by not more than 3%.

TABLE 2. *Activity coefficients of methyl iodide in carbon tetrachloride at* 298·16° K.

c_2 (mole/l.)	0	0·1	0·2	0·3	0·4
γ_2	1	0·9965	0·9862	0·9794	0·9728

Solutions of Trimethylamine in Carbon Tetrachloride.—Because of the wide difference between the vapour pressures of these two liquids, the standard method of studying the vapour–liquid equilibria is unsuitable, and was replaced by a method which depended on the direct chemical analysis of the composition of the two phases. The distribution vessel consisted of two compartments (*A* and *B*, Fig. 1) separated by a hollow tap (*C*) and surrounded by double surfaces between which thermostat water was vigorously pumped. The tap *C* was so constructed that the two compartments could be connected by means of a glass passage. When the tap is turned through 180°, access to compartment *A* was possible *via* the opening *E* and a hole *D* in the inner wall of the tap. Tap *C* is first filled with clean mercury and the clamp on opening *E* is closed. The cell is evacuated, and an appropriate amount of carbon tetrachloride is introduced, and boiled to remove traces of dissolved gases. The cell is joined to a vacuum-system through a yard of coiled copper tubing of 1·5 mm. bore, and is clamped horizontally in a cradle which can be violently rocked. Trimethylamine is cautiously admitted from a gas burette, and the pressure of the equilibrated system is finally measured against a mercury manometer. The distribution cell is allowed to remain vertical until all the liquid has drained from compartment *A*. By careful manipulation of the taps *J* and *E* it is possible to flood both compartments separately with a known excess of aqueous nitric acid. The amount of amine in either compartment is then calculated after back titration with alkali. The partial pressure of the amine was calculated in mm. of Hg by using Berthelot's equation

FIG. 1. *Vapour–liquid distribution cell.*



$$p = \frac{\nu \boldsymbol{R} T}{V}\left\{1 + \frac{9}{128}\frac{T_c}{T}\frac{p}{p_c}\left[1 - 6\left(\frac{T_c}{T}\right)^2\right]\right\} \quad . \; . \; . \; . \; . \; . \; . \quad (8)$$

where ν is the number of moles of amine in V c.c. of the vapour, $\boldsymbol{R}$ = 63,380 in these units, T_c = 433·3° K, and p_c = 40·24 atm.[7]

At 273·41° K experiments were made on mixtures of all compositions, but at 298·18° K and 317·86° K only with solutions containing not more than 0·5 mole-fraction of amine. The interchange energy calculated according to equation (3) was found to be neither zero nor constant. Solutions of trimethylamine in carbon tetrachloride are, therefore, neither ideal nor regular. Somewhat similar behaviour has been reported for the methanol–carbon tetrachloride system by Scatchard and Ticknor,[8] who found it necessary to use five constants to represent the excess free energy of the solution over that of an ideal solution. Our results are not sufficiently accurate to justify such a detailed analysis, and we shall content ourselves with recording interpolated values of the activity coefficients reckoned on a mole-fraction basis (Table 3). It

TABLE 3. *Activity coefficients of trimethylamine in carbon tetrachloride solution at* 298·16° K.

x_3	0	0·01	0·02	0·03	0·04	0·06	0·08	0·10	0·20	0·30	1·00
p_3 (mm.)	0	18	33	46	58	83	109	137	290	486	1663
γ_3	(1·70)	1·08	0·99	0·92	0·87	0·83	0·82	0·82	0·87	0·97	1·00

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[7] Day and Felsing, *J. Amer. Chem. Soc.*, 1950, **72**, 1698.
[8] Scatchard and Ticknor, *ibid.*, 1952, **74**, 3724.

will be observed that, with increasing concentration, the activity coefficient of the amine decreases rapidly until it reaches a minimum value at a molar fraction of about 0·09. The extrapolated value of γ_3 at zero concentration, obtained from a logarithmic plot, is a conservative estimate. Experimental values exceeding 2 were obtained for some of the very dilute solutions. Most of our kinetic experiments were done with solutions of trimethylamine containing not more than 0·1 mole per l., corresponding to molar fractions not exceeding 0·01. During the course of the reaction, therefore, the activity coefficient of the amine rises continuously.

Solutions of Tetramethylammonium Iodide in Carbon Tetrachloride.—Repeated agitation of the finely ground salt with the pure solvent in sealed tubes at 25° showed that the salt was insoluble within the accuracy of the analytical estimation, which was 0·2 mmole per l. Solubility measurements with the pure salt and the pure solvent were then for a time discontinued. Chemical analysis of the products of the reaction between methyl iodide and trimethylamine in carbon tetrachloride solution, however, revealed the undoubted presence of inorganic iodide. It was therefore concluded that the salt, though insoluble in the pure solvent, was soluble in solutions of the products of its own decomposition. Separate experiments with solutions of either methyl iodide or trimethylamine in carbon tetrachloride proved this to be true. The results at 298·16° K are shown graphically in Fig. 2. It is impossible from these data to extrapolate a value for the solubility of the salt in the pure solvent, though it may safely be assessed as not more than 1 × 10^{-4} mole/l. Vernon and Sheard [9] have measured the solubility of tetramethylammonium iodide in mixtures of ethylene dichloride and benzene. Using an empirical relation between the solubility of the salt and the dielectric constant of the mixed solvent, they estimated its solubility in pure benzene as 6·92 × 10^{-6} mole/l. As the dielectric constants of benzene and carbon tetrachloride at this temperature are very similar (2·253 and 2·219), our conclusion seems to be indirectly confirmed. The analyses of reaction products given in Table 4 indicate an approximate value of 0·022 l./mole for the term $s/(a - x_\infty)(b - x_\infty)$, where s is the concentration of salt in solution, and $a - x_\infty$ and $b - x_\infty$ are the final concentrations of methyl iodide and trimethylamine respectively in the homogeneous phase. Clearly, if we start with a solution containing equimolar proportions of the reactants at concentrations of 0·1M, chemical reaction proceeds about 96% of the way. Lower values of $s/(a - x_\infty)(b - x_\infty)$ were obtained in more dilute solutions, but the internal consistency of the analyses was less satisfactory than in Table 4.

FIG. 2.

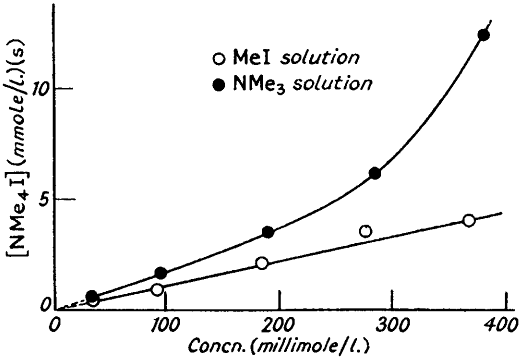

TABLE 4. *Compositions of final solutions (mmoles/l.) at* 298·16° K.

$a = [CH_3I]_0$	$b = [NMe_3]_0$	$a - x_\infty$	$b - x_\infty$	s
97·2	37·7	59·6	0·5	0·7
105·6	106·0	4·3	4·8	0·4
174·5	37·7	137·6	0·3	1·0

Kinetic Procedure.—Solutions of methyl iodide were made in a conical flask connected by a ground-glass join to a tap and thence to a B7 cone; the solute was introduced from a weight pipette into the pure solvent under its own vapour pressure and at the run temperature.

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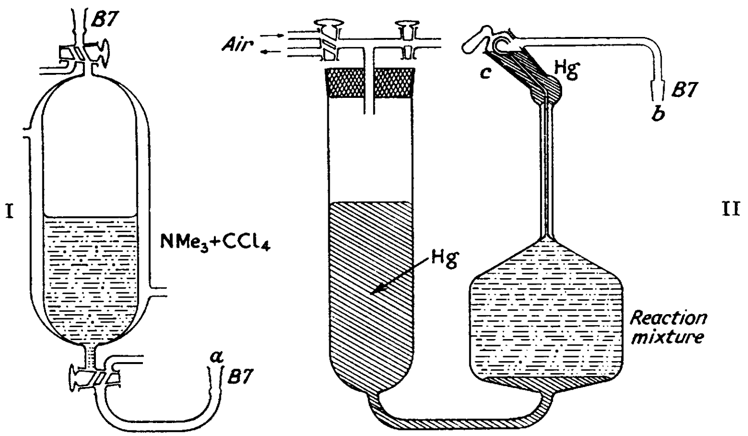
[9] Vernon and Sheard, *J. Amer. Chem. Soc.*, 1948, **70**, 2035.

Solutions of trimethylamine were prepared in vessel I (Fig. 3) by leading in the vapour at a regulated pressure from a gas-burette as in the distribution experiments. The solutions were mixed through the B7 joints and were drawn into vessel II (Fig. 3) which was included in the thermostat. At suitable time intervals 5 ml. of the mixture were expressed through tap *C* into a known excess of ice-cold aqueous nitric acid. Samples drawn from the early stages of reaction were analysed for free base by titration with hydriodic acid, and for iodide ion by titration with potassium iodate. After crystals had appeared in the reaction vessels, samples were expressed through a plug of glass-wool, and only the base was estimated. The total amount of organic and inorganic iodide in initial and final samples was estimated after digestion for 10 hr. at 100° with excess of sodium methoxide in methanol solution.

FIG. 3.



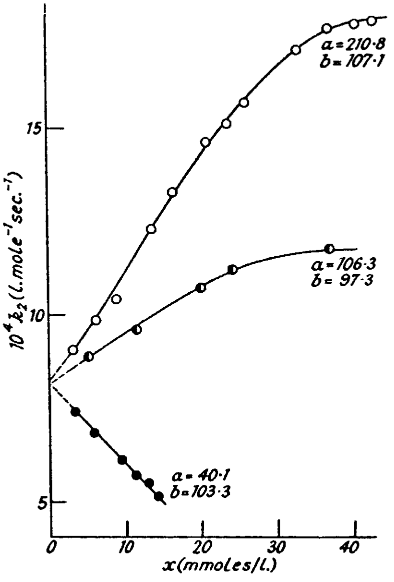


FIG. 4. *Second-order velocity coefficients at* 298·23° K.

Kinetic Results.—Experiments were carried out in duplicate and, unless the two agreed, in triplicate. The numerous runs at 298·23° K showed that the second-order velocity coefficients calculated from the equations

$$\frac{dx}{dt} = k_2(a - x)(b - x)\ ; \quad k_2 = \frac{1}{t(a - b)} \ln \frac{b(a - x)}{a(b - x)} \quad . \quad . \quad . \quad . \quad (9)$$

varied during the run. With methyl iodide in excess, k_2 increased with time; with trimethylamine in excess, k_2 decreased with time. The results of a typical run are shown in Table 5, and the general behaviour in Fig. 4. It is clear that the anomalies noted by Grimm, Ruf, and Wolff[2] and by Moelwyn-Hughes and Hinshelwood[3] persist even when there is no vapour phase present.

TABLE 5. *Second-order velocity coefficients at* 298·23° K. $a = 210{\cdot}8 \pm 0{\cdot}8$; $b = 107 \pm 1{\cdot}7$.

t (min.)	x (mmoles/l.)	Change (%)	$k_2 \times 10^4$ (l. mole^{-1} sec.$^{-1}$)	t (min.)	x (mmoles/l.)	Change (%)	$k_2 \times 10^4$ (l. mole^{-1} sec.$^{-1}$)
0	0	0	—	35	47·1	44·0	15·0
5	5·8	5·4	9·10	40	52·5	49·0	15·6
10	12·2	11·4	9·88	55	65·9	61·5	17·0
15	18·2	17·0	10·3	70	75·1	70·1	17·6
20	26·9	25·1	12·3	85	81·3	75·9	17·7
25	34·1	31·8	13·3	100	86·7	80·5	17·8
30	41·6	38·6	14·6	∞	107·1	100·0	—

DISCUSSION

To interpret these kinetic observations is not easy, even with the help of all the ancillary static determinations.

That tetramethylammonium iodide, though insoluble in pure carbon tetrachloride, is soluble in it when it also contains either methyl iodide or trimethylamine is consistent with the observation that the early stages of each kinetic run take place in the homogeneous liquid phase. In principle, a decrease in the value of k_2 can be attributed to the reverse reaction, and equation (9) can be modified as follows :

$$\mathrm{d}x/\mathrm{d}t = k_2(a - x)(b - x) - k_1 x \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where x is the concentration of the salt in solution. After the appearance of crystalline salt, the kinetic law becomes

$$\mathrm{d}x/\mathrm{d}t = k_2(a - x)(b - x) - k_1 s \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where s is its solubility. On integrating we have :

$$k_2 = \frac{1}{2\beta t} \ln \left\{ \frac{1 - [x/(\alpha + \beta)]}{1 - [x/(\alpha - \beta)]} \right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where $\alpha = \frac{1}{2}(a + b) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$

and $\beta^2 = [\frac{1}{2}(a + b)]^2 - ab + (k_1/k_2)s \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$

On using the data of Table 4 we find that the calculated effect of the reverse reaction is less than the observed effect. It is possible that s varies with the course of reaction. This is a point which would be extremely difficult to prove or to disprove experimentally. Fig. 2, of course, merely shows the effect of the solutes separately on the solubility of the salt. Two explanations can be offered for the increase in k_2 shown by solutions containing equimolar concentrations of the two solutes, or methyl iodide in excess of methylamine :

(1) The rate-determining reaction, even in the presence of the salt, may be assumed to proceed in the homogeneous liquid phase; and its rate may be assumed to be governed by the activities of the two reactants. Then, as shown in Tables 2 and 3, though the activity coefficient of the halide remains sensibly constant, that of the amine increases as its concentration diminishes. Velocity coefficients calculated by means of the incremental equation

$$k_2 = \frac{1}{(a - x)\gamma_2(b - x)\gamma_3} \cdot \frac{\mathrm{d}x}{\mathrm{d}t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

were, on the whole, less variable than those calculated by means of equation (9). For example, the run shown in the centre of Fig. 4 gives, in terms of activities, an initial and fairly constant value of $k_2 \times 10^4 = 8{\cdot}14$, which ultimately falls to 6·85.

(2) It can be assumed that, after the appearance of crystals, the homogeneous reaction is accompanied by a heterogeneous reaction at the surface of the crystals and involving the adsorption of either solute or of both.

On the whole the second explanation is preferred because it does not rely on the illogical assumption, so often made in chemical kinetics, that γ_3 as measured for a single solute in solution is identical with its value in the presence of a second solute. If the catalytic effect were proportional to the extent of reaction, we would have, in terms of concentrations, the rate equation

$$dx/dt = k_2(a - x)(b - x) + k_3(a - x)(b - x)x \quad . \quad . \quad . \quad . \quad (16)$$

or

$$(k_2 + k_3b)t = \frac{1}{(a - b)} \ln\left[\frac{b(a - x)}{a(b - x)}\right] + \frac{1}{(a + c)} \ln\left[\frac{a(c + x)}{c(a - x)}\right] \quad . \quad . \quad (17)$$

where

$$c = k_2/k_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Equation (16), however, can only account for the positive gradients in Fig. 4, and it is clear that the catalytic effect, which is proportional to the area of the crystalline surface, cannot be a linear function of x. The differential rate law based on equations (11) and (16) describes the general features of the somewhat complicated kinetics:

$$dx/dt = k_2(a - x)\gamma_2(b - x)\gamma_3 - k_1s + k_3(a - x)\gamma_2(b - x)\gamma_3 f(x) \quad . \quad . \quad (19)$$

An apparently second-order reaction can thus emerge owing to the cancellation of the second and the third term.

Influence of Temperature.—From measurements made at temperatures above and below 298·23° K, estimates can be made of the constants A and E_A of the integrated form of Arrhenius's equation

$$k_2 = A \exp\,(-E_A/RT) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Because of the relatively early deposition of crystals, these constants can only be evaluated for the heterogeneous reaction. They show (Table 6) an apparent decrease with the extent of reaction, of a magnitude which can be ascribed to adsorption of either solute on the crystal surface. In view of the complexity of the reaction, no simple interpretation of these constants can be given. If they are in fact constant, the rate of reaction between methyl iodide and trimethylamine at 100° C must be about 500 times as fast as that between the corresponding ethyl compounds in the same solvent. It is possible, however, as Tommila and Kauranen [10] have pointed out, that they are both functions of temperature. When their observations at 325·7° K and those of Grimm, Ruf, and Wolff at 368·2° K are combined and given equal weight, the apparent energy of activation of the reaction between methyl iodide and trimethylamine in benzene solution becomes

TABLE 6. *Arrhenius constants at* 298·16° K.

x (mmoles/l.)	10	20	30
E_A (cal./mole)	9760	8740	8280
A (l. mole^{-1} sec.$^{-1}$)	$1·33 \times 10^4$	$2·68 \times 10^3$	$1·39 \times 10^3$

$$E_A = (18{,}250 \pm 3250) - (9·35 \pm 4·75)RT$$

Menschutkin's reaction thus appears to resemble numerous other reactions in solution. To gain more precise information on the kinetics of these reactions in the homogeneous liquid phase, a new technique is required and is now being developed.

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[10] Tommila and Kauranen, *Acta Chem. Scand.*, 1954, **8**, 1152.