Liquid-phase Reactions at High Pressures. Part VIII.[*] *The Kinetics of an* " ortho-*Effect* " *Reaction at High Pressures.*

By K. E. WEALE.

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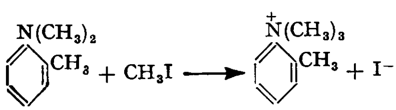
The rate of the reaction between methyl iodide and *o*-methyl-*NN*-dimethylaniline in dry methanol has been measured up to 5000 atmospheres at four temperatures. This reaction, which exhibits the " *ortho*-effect," is accelerated by pressure. The changes in the Arrhenius parameters, *A* and *E*, are, however, the reverse of those found for unhindered Menschutkin reactions, which are also accelerated by pressure. It is concluded that a new effect is operative, and that pressure assists this reaction by reducing steric strain in the transition state.

AT hydrostatic pressures of several thousand atmospheres the rates of many liquid-phase reactions are considerably increased. Previous measurements (Perrin, *Trans. Faraday Soc.*, 1938, **34**, 144; Newitt, Sapiro, *et al.*, Parts III and V, *J.*, 1938, 784; 1939, 1761) have shown that the acceleration is greatest for the so-called "slow" reactions, in which the *A* term of the Arrhenius equation, $k = Ae^{-E/RT}$, is smaller by several powers of ten than the value ($\sim 10^{12}$) characteristic of " normal " reactions.

Rate determinations have now been carried out at high pressures on a "slow" reaction of a type which is retarded at ordinary pressure by the " *ortho*-effect." This is the Menschutkin reaction between methyl iodide and *o*-methyl-*NN*-dimethylaniline in dry methanol, which was investigated, with others, by Evans, Watson, and Williams (*J.*, 1939, 1345, and 1348) who find that the second-order rate constant at 65° is lower by a factor of 61 than that for the reaction with the corresponding *p*-substituted amine at the same temperature. The decreased reaction velocity of the *ortho*-derivative is due to an increase of 6·6 kcal./mole in the activation energy *E* which outweighs an accompanying 250-fold increase in *A*.



EXPERIMENTAL

Apparatus.—The equipment for producing pressures up to 5000 atm. has been described by Newitt *et al.* (*J.*, 1938, 784). The pressure vessel is a steel, compound-shrunk cylinder which is immersed in an oil-bath maintained at a constant temperature to within ±0·1°. It is sealed at the top by a hard-rubber closure and a steel screw-plug. Steel capillary tubing leads from the base to a piston intensifier with an effective intensification ratio of 9·1 : 1, and the pressure-transmitting medium is liquid paraffin, which completely fills the apparatus. The Pyrex-glass reaction tube (capacity 4—5 ml.), closed at the top by a ground-glass stopper and open at the bottom, floats on mercury in a steel holder. The mercury transmits pressure to the reactants and prevents contamination by the oil.

Materials.—" AnalaR " methanol was dried by the Lund–Bjerrum magnesium method (*Ber.*, 1931, **64**, 210), fractionated in a Widmer column (b. p. 64·2—64·5°/760 mm.), and stored in a desiccator. Methyl iodide and *o*-methyl-*NN*-dimethylaniline were treated as described by Evans, Watson, and Williams, and fractionated at normal pressure (b. p. 42·5° and 184—185°, respectively). 0·2M-Solutions of each reactant in methanol were stored in 100 ml. stoppered flasks in a desiccator in the dark.

Kinetic Measurements.—5 ml. of each methanolic solution were mixed and the reaction tube was filled and put in the holder which was then enclosed in the pressure vessel (already at a constant temperature); pressure was then developed by means of the oil hand-pump and intensifier. This operation took 1—2 min., and the time of a run was usually 300—500 min. Pressure was measured on the low-pressure side of the intensifier by a Bourdon-tube gauge calibrated against a free-piston gauge. The pressure in the reaction vessel was calculated from the effective ratio of the intensifier, also calibrated by a free-piston gauge. The accuracy of the pressure measurement was about 0·1%, and the pressure was held constant within ±1%.

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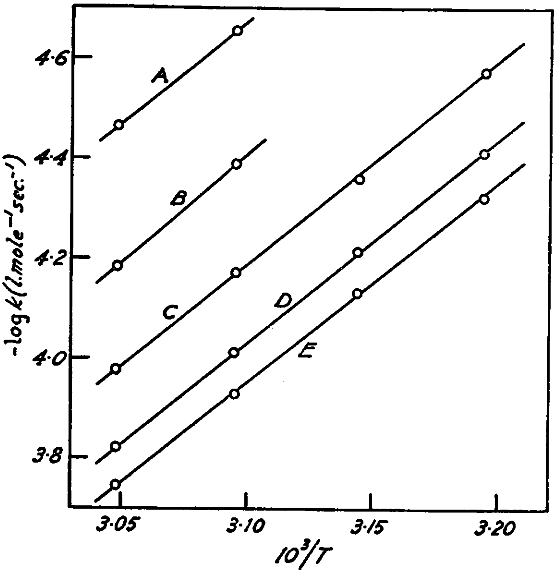
[*] Part VII, *J.*, 1952, 2223.

At the end of a run, the pressure was reduced quickly to 1 atm. and the solution removed. 2 ml. were added to 25 ml. of " AnalaR " light petroleum (b. p. 40—60°) and extracted three times with 10 ml. portions of distilled water. The aqueous extract was acidified with 5—10 drops of dilute acetic acid, and titrated with 0·01N-silver nitrate (eosin).

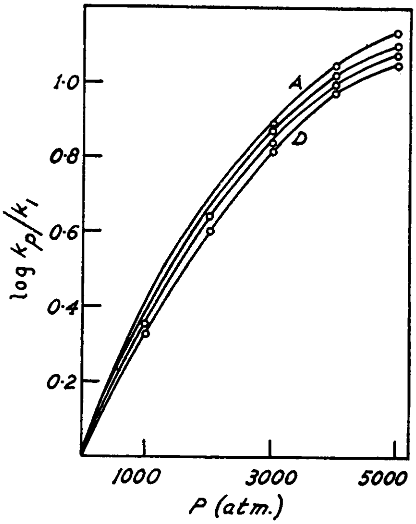
Several runs were carried out at each pressure and temperature. Bimolecular rate constants were calculated and average values taken. The maximum variation in k was generally 2—3%. Runs carried out with the addition of a drop of water (about 0·05% by weight) did not give significantly different rates, showing that the reaction is not sensitive to small amounts of moisture.

FIG. 1.



Curves A—E at 1000, 2000, 3000, 4000, *and* 5000 *atm. respectively.*

FIG. 2.



Curves A—D at 40°, 45°, 50°, *and* 55° *respectively.*

Results.—The rate constants were measured at 1000 atm. intervals up to 5000 atm., at 40°, 45°, 50°, and 55°, except that at the lowest two pressures the reaction was sufficiently fast only at 50° and 55°.

The velocity constant k_1 was also measured in the same apparatus at 1 atm. at 50°. The result, together with Evans, Watson, and Williams's values at 65°, 90°, and 100°, gives a good straight line for log k against $1/T$. Velocity constants at 1 atm. for the other three reaction temperatures were taken from this line.

TABLE 1. *Bimolecular velocity constants* (*l. mole*$^{-1}$ *sec.*$^{-1}$) $\times 10^5$, *at various pressures and temperatures.*

Temp.	40°	45°	50°	55°
Velocity constant at 1 atm., k_1	0·347	0·587	0·986	1·61

Temp.	k'	k	k_p/k_1
	1000 atm.		
50°	2·41	2·22	2·25
55	3·76	3·45	2·14
	2000 atm.		
50°	4·70	4·11	4·17
55	7·38	6·43	3·99
	3000 atm.		
40°	3·15	2·67	7·69
45	5·18	4·38	7·46
50	8·02	6·77	6·87
55	12·5	10·5	6·55
	4000 atm.		
40°	4·71	3·88	11·2
45	7·49	6·15	10·5
50	11·9	9·75	9·89
55	18·6	15·2	9·41
	5000 atm.		
40°	5·79	4·78	13·8
45	8·94	7·39	12·6
50	14·2	11·8	12·0
55	21·7	18·1	11·2

All the rate constants have been corrected for thermal expansion, and for the isothermal compression of the solvent at the reaction temperature (about 15% at 5000 atm.). The compression data used were those of Bridgman (*Proc. Amer. Acad. Arts Sci.*, 1913, **49**, 3), which may be slightly too low (Gibson, *J. Amer. Chem. Soc.*, 1935, **57**, 1551), but not enough to affect this correction. The results are shown in Table 1, where k' is the temperature-corrected constant, and k is the final value corrected for compression. k_p/k_1 is the ratio of the rate constant at high pressure to that at 1 atm.

In Fig. 1, $\log_{10} k$ is plotted against $1/T$. Except for 1000 and 2000 atm. the straight lines have been fitted by the method of least squares, and the corresponding Arrhenius parameters are given in Table 2. The effect of pressure on E and A is always to diminish them, although the variation of each with pressure is not quite regular because of experimental error. The accelerating effect falls off markedly at high pressures as is illustrated in Fig. 2, where $\log_{10} k_p/k_1$ is plotted against P.

TABLE 2. *Arrhenius parameters at various pressures.*

P (atm.)	1	1000	2000	3000	4000	5000
$\log_{10} A$	9·129	(8·0)	(8·4)	8·40	8·53	7·97
E (kcal./mole)	20·89	(18·7)	(18·9)	18·57	18·53	17·60

(The figures at 1000 and 2000 atm. are obtained from rates at two temperatures only.)

DISCUSSION.

The reaction studied is accelerated by pressure to much the same extent as are others of the Menschutkin type examined by Perrin and his co-workers. There is, however, a notable difference in the effect on A and E. In each of seven reactions Perrin finds the increase in rate to be due to a large increase in A (up to 111-fold at 3000 atm.), which outbalances a simultaneous increase in E (up to 1·4 kcal. at 3000 atm.). In the present case, on the contrary, there is a considerable decrease in E, which is partially offset by a decrease in A. This reversal of behaviour among reactions of similar type is thought to indicate a fundamental difference in the way in which pressure influences the reaction rate.

The "Transition-density" Theory.—The effect of hydrostatic pressure on the rate of reaction in a liquid has been related to the volume change ΔV^*, accompanying formation of the transition state, by the equation :

$$\partial \log k/\partial P = \Delta V^*/\boldsymbol{R}T$$

(Evans and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 875; 1936, **32**, 1333; Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, 1941; Stearn and Eyring, *Chem. Reviews*, 1941, **29**, 509). ΔV^* may be obtained at any pressure from the slope of the curve relating $\log k_p/k_1$ to P, which for some reactions is a straight line. The pressure dependence of the reaction rate thus gives information about the density of the transition state, as the temperature dependence gives the energy. Evans and Polanyi pointed out that ΔV^* includes a term representing the different amount of interaction of the solvent with the reactants and with the transition state. This aspect has been re-emphasised by Buchanan and Hamann (*Trans. Faraday Soc.*, 1953, **49**, 1425), and in Menschutkin reactions, in which charge separation occurs, with consequent electrostriction of solvent molecules, the solvation term may predominate.

The reversed effect of pressure on E and A, which shows the operation of a new factor in the "*ortho*-effect" reaction, is not readily explicable by means of the "transition-density" theory.

*The Nature of the "*ortho*-effect."*—Evans, Watson, and Williams could find no connection between the magnitude of the "*ortho*-effect" in Menschutkin reactions and the weights, volumes, or chemical characters of different substituent groups. Considering also the absence of a large "*ortho*-effect" in the basic strengths of the isomeric methyl-*NN*-dimethylanilines, Watson suggested that the effect is only operative in the highly energised transition state, and that it is due to interaction of the *ortho*-group with the unshared nitrogen electrons. The interaction may vary from near zero (*o*-fluoro) to proton-transfer with electrovalent bonding (*o*-carboxyl). In the case of the *o*-methyl group, Watson assumes hydrogen-bond formation with the nitrogen atom. W. G. Brown and Fried (*J. Amer. Chem. Soc.*, 1943,

65, 1841), however, correlate Watson's sequence of the relative "*ortho*-effects" of different substituent groups with their effectiveness in preventing rotation in the diphenyl series. They suppose that the *N*-methyl groups and the aromatic ring have to become coplanar in the transition state, and that the "*ortho*-effect" is due to steric hindrance in this configuration. Confirmatory evidence is provided by the absence of the effect in the reactions of bicyclic tertiary amines, in which the groups are constrained into coplanarity.

H. C. Brown (Brown and Barbaras, *J. Amer. Chem. Soc.*, 1947, **69**, 1137; Brown and Eldred, *ibid.*, 1949, **71**, 445; Brown and Cahn, *ibid.*, 1950, **72**, 2939) also supports a steric rather than a polar interpretation. The absence of a large "*ortho*-effect" in the base strengths is attributed to the small steric requirements of the proton, and the differences of stability found among the compounds of trimethylboron with pyridine and the picolines show that the "*ortho*-effect" does appear in equilibria. Brown and Barbaras conclude that the slowness with which *ortho*-substituted compounds participate in displacement reactions is due to steric strain in the transition state. This strain will result in an increased activation energy, as was found in the sterically hindered S_N2 reactions of *neo*pentyl halides by Dostrovský, Hughes, and Ingold (*J.*, 1946, 157 *et seq.*).

The Acceleration of the "ortho-*Effect*" *Reaction by Pressure.*—The alterations in *A* and *E* caused by pressure are such as to oppose the increase in these parameters, which occurs at ordinary pressure when one changes from the *para*- to the *ortho*-substituted amine. They are the reverse of the pressure effects found for the Arrhenius parameters of unhindered Menschutkin reactions. For these reasons it is concluded that in the "*ortho*-effect" reaction the compression energy of the liquid system is able to contribute directly to lowering the activation energy by overcoming steric strain in the transition state. The "steric strain" effect, and not that of "transition-density," is the principal factor causing an increase in the rate constant.

DEPARTMENT OF CHEMICAL ENGINEERING AND APPLIED CHEMISTRY,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
S. KENSINGTON, LONDON, S.W.7.

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