150. *Liquid-phase Reactions at High Pressures. Part III. The Esterification of Acetic Acid.*

By SHU-LIN P'ENG, R. H. SAPIRO, R. P. LINSTEAD, and D. M. NEWITT.

The rate of esterification of acetic acid with a series of primary and secondary aliphatic alcohols has been measured at pressures from 1 to 4000 atmospheres, and at temperatures between 70° and 80°. The velocity constants for the *n*-primary alcohols are all of the same order, tending, if anything, to diminish as the series is ascended; *iso*propyl and *sec.*-butyl alcohols have much lower constants than the primary alcohols.

The accelerating effect of pressure becomes less marked on ascending the series of primary alcohols; it is greater for *iso*- and *sec.*-alcohols than for primary alcohols.

For all the reactions studied, the constants A and E of the Arrhenius equation ($k = Ae^{-E/RT}$) increase with pressure, the effect being greatest with *iso*propyl and *sec.*-butyl alcohols. The cause of this increase is discussed, and it is shown that although the increase in A can, in some instances, be accounted for by an increase in the collision frequency with pressure, yet in other cases the probability that collisions between molecules possessing the requisite amount of energy will result in reactions is also increased. A functional relationship is found to exist between A and E.

IN Part I (Newitt, Linstead, Sapiro, and Boorman, J., 1937, 876) it was shown *inter alia* that the rate of esterification of acetic acid with ethyl alcohol was greatly accelerated by increase of hydrostatic pressure; *e.g.*, at 6500 atm. the system passes more than half-way to equilibrium under conditions which give only a very small amount of esterification at atmospheric pressure.

The effect of pressure upon a similar esterification, *viz.*, that of acetic anhydride with ethyl alcohol in dilute alcoholic and toluene solutions, severally, has been investigated by Williams, Perrin, and Gibson (*Proc. Roy. Soc.*, 1936, *A*, **154**, 684), who also observed a marked increase in the rate of reaction with pressure; by applying the reaction-velocity equation $k = PZe^{-E/RT}$ to their results (Z being evaluated by the gas collision formula), they showed that the experimental value of the velocity constant is several powers of ten less than the calculated value. In conformity with all other " slow " reactions in like circumstances, the pressure effect in toluene solution is to cause an apparent increase in the activation energy, E, and a more than compensating increase in the value of the product PZ. In alcoholic solution, on the other hand, both E and PZ decrease with increasing pressure although the net effect of pressure on the rate is of the same order as in the toluene solution; they suggest that " some complicating factor due to the effect of pressure on the collision rate " may afford an explanation of this difference in behaviour.

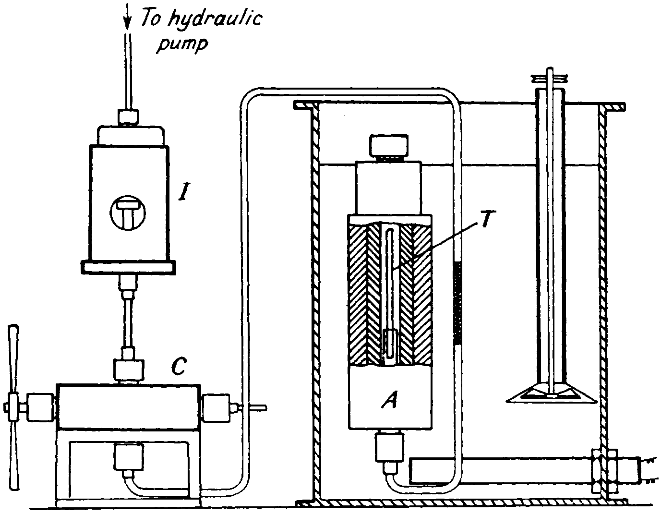
In this connexion it may be pointed out that some uncertainty attaches to the value of the collision number Z in the case of liquid-phase reactions; if the gas-kinetic value is accepted then the probability factor P is found to vary from reaction to reaction between the limits 1 and 10^{-11}; for a given reaction it may also vary from solvent to solvent or with change of hydrostatic pressure. There is, moreover, reason to believe that collisions between pairs of molecules of different species, leading to interaction in dilute solution, are of a special kind, differing not only from those in the gas-phase but also from those occurring in a mixture of two miscible liquids in the absence of a solvent (Rabinowitch and Wood, *Trans. Faraday Soc.*, 1936, **32**, 1381). To obtain further information upon these matters we have re-examined in more detail the esterification of acetic acid, and have extended the scope of the earlier work so as to include a series of primary and secondary alcohols. Both in the original experiments and in those described below, only the pure reactants were used, in equimolecular proportions, so that, although the data are unaffected by any purely solvent action other than that arising from the reaction products, they would be expected to show the influence of changes in the compressibility, viscosity, and thermal expansion of the medium due to changes in the hydrostatic pressure.

EXPERIMENTAL.

The method of developing and maintaining hydrostatic pressures of the order of 5000 atm. has been described in Part I (*loc. cit.*). In view of the requirements of the present experiments, however, a rearrangement of the apparatus was necessary (see Fig. 1) in order to enable the reaction vessel to be completely immersed in a constant-temperature bath. The steel reaction vessel, A, is connected through the valve C to an intensifier, I, by means of which its contents can be raised to the required pressure. The reactants are contained in a glass tube, T, over mercury, and pressure is applied through the medium of liquid paraffin, which completely fills the free space in the reaction chamber. In all experiments the pressure was raised at a uniform slow rate to allow sufficient time for the dissipation of the heat of compression.

" AnalaR " Reagents were employed. Acetic acid was recrystallised four times. The alcohols were dried over metallic calcium and subsequently fractionated, through a 3-ft. column, the fractions distilling within a narrow range of the accepted b. p.'s being collected. The mercury was purified by agitation with dilute nitric acid, washing with distilled water, and distillation in a vacuum.

FIG. 1.



The glass reaction vessels were treated with warm chromic acid, followed by repeated washings with distilled water. As there is a possibility of some solvent action on the glass at high pressures resulting in catalytic action, a number of comparative experiments were carried out in glass and transparent silica vessels of the same linear dimensions. In no case was any appreciable difference in the rate of esterification observed; *e.g.*, in the esterification of acetic acid with *n*-propyl and *n*-butyl alcohol, respectively, the following data were obtained :

	Values of $k \times 10^7$ at 80° from experiments in (1) a glass vessel.	(2) a silica vessel.
n-Propyl alcohol	131·5	135·9
n-Butyl alcohol	128·8	127·0

The agreement is well within the experimental error.

The initial acid–alcohol mixtures were made up by weight immediately before each experiment. The percentage esterification was determined by titration of the free acid, followed by hydrolysis of the ester with an excess of standard alkali. The velocity constants, *k*, were calculated from the simple bimolecular expression, corrections being made for the changes in concentration due to the compressibilities and thermal expansions of the reactants. For the various alcohols, Bridgman's compressibility data were employed; for acetic acid no data are available, and in order to make the correction a value intermediate between that of ethyl alcohol and ethyl acetate has been assumed.

In the tabulated results (Table I) the corrected values of *k* are given in the units l./g.-mol.-sec.

The constants for the *n*-primary alcohols are all of the same order, tending, if anything, to diminish as the series is ascended; *iso*propyl and *sec.*-butyl alcohols have comparatively low constants, but those of *iso*butyl alcohol, which contains the primary $-CH_2OH$ group, are high. In Fig. 2, $\log_{10}k-1/T$ isobars for the various alcohols at 3000 atm. are shown, together with (inset) isobars for ethyl alcohol at 1, 2000, 3000, and 4000 atm. In all cases a satisfactory linear relationship is exhibited.

The effect of pressure (k_p/k_1) is most marked in the case of ethyl and *sec.*-butyl alcohols, and is least so for *iso*butyl alcohol; for the primary alcohols k_{3750}/k_1 diminishes on ascending the series from 17·9 for ethyl alcohol to 12·8 for *n*-butyl alcohol. In general, the order of the effect is greater than for reactions of the same type in dilute solution; *e.g.*, according to Williams, Perrin, and Gibson (*loc. cit.*), k_p/k_1 for the esterification of acetic anhydride with ethyl alcohol in toluene solution, at 30° and over the same pressure range, is only about 7. It will also be observed that the pressure effect shows a slight but definite increase with increase of temperature.

TABLE I.

Velocity Constants for the Esterification of Acetic Acid with a Series of Alcohols at Pressures between 1 and 4000 Atmospheres.

	Pressure, atm.								
	1.	2000.		3000.		3750.		4000.	
Temp.	$k_1 \times 10^7$.	$k_p \times 10^7$.	k_p/k_1.	$k_p \times 10^7$.	k_p/k_1.	$k_p \times 10^7$.	k_p/k_1.	$k_p \times 10^7$.	k_p/k_1.
				Ethyl alcohol.					
50°	2·34	12·35	5·28	25·63	10·9	—	—	60·01	25·7
60	4·20	20·88	4·97	47·92	11·4	—	—	101·35	23·6
70	7·98	41·42	5·19	81·30	10·2	—	—	193·80	24·2
75	12·70	58·10	5·33	125·00	11·5	227·5	17·9	—	—
				n-Propyl alcohol.					
70	10·04	41·80	4·14	81·30	8·10	136·00	13·5		
75	13·28	56·22	4·23	108·40	8·16	182·40	13·7		
80	17·82	77·05	4·32	144·60	8·11	254·00	14·2		
				n-Butyl alcohol.					
70	10·41	37·20	3·58	74·20	7·14	123·0	11·8		
75	13·07	51·88	3·97	100·40	7·70	167·0	12·8		
80	17·27	73·70	4·28	145·20	8·42	226·0	13·1		
				*iso*Propyl alcohol.					
70	2·44	9·37	3·84	18·59	7·62	30·84	12·6		
75	3·31	14·13	4·37	28·84	8·72	49·10	14·8		
80	4·40	20·97	4·76	44·26	10·10	77·80	17·7		
				*iso*Butyl alcohol.					
70	20·55	53·98	2·63	88·10	4·29	128·2	6·25		
75	28·19	77·69	2·72	131·20	4·66	191·6	6·79		
80	39·20	116·00	2·96	188·40	4·81	279·7	7·09		
				sec.-Butyl alcohol.					
70	1·77	9·68	5·46	20·66	11·65	36·22	20·45		
75	2·68	14·13	5·27	31·75	11·85	57·60	21·50		
80	3·89	21·14	5·44	49·20	12·64	90·50	23·30		

From the data in Table I the values of the activation energy, E, and the constant, A, of the Arrhenius equation ($k = Ae^{-E/RT}$) for the various pressures have been calculated and are summarised in Table II. For all the reactions studied both E and A increase with pressure, the effect being greatest with *iso*propyl and *sec.*-butyl alcohols; the activation energies of the *n*-primary alcohols increase progressively on ascending the series at all pressures above atmospheric.

TABLE II.

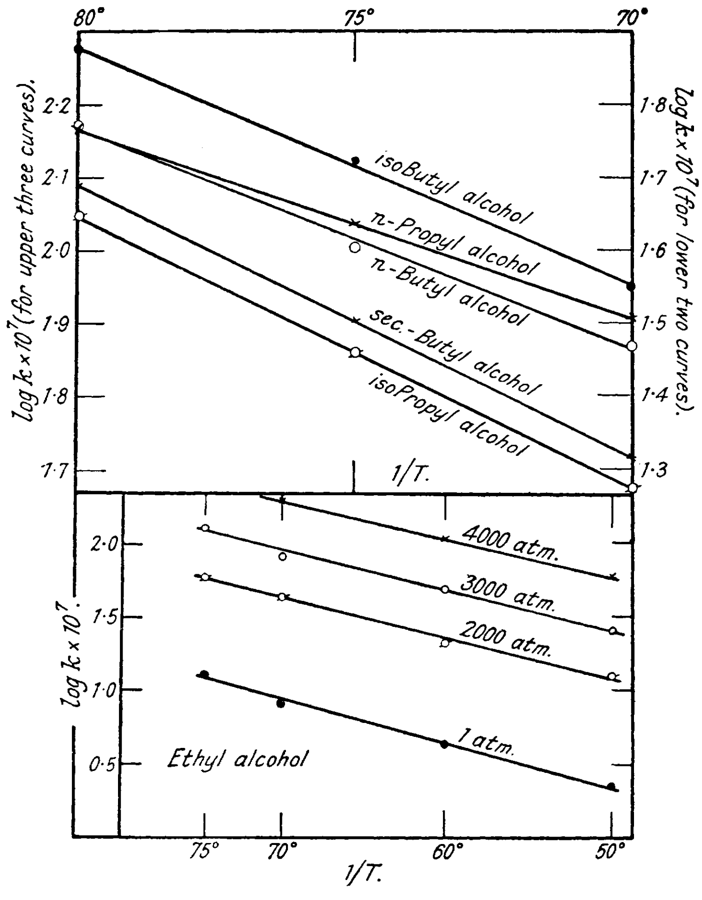
Values of the Constants of the Arrhenius Equation for the Rate of Esterification of Acetic Acid with a Series of Alcohols.

Alcohol.	Press., atm.	E, cals.	A or PZ.	Alcohol.	Press., atm.	E, cals.	A or PZ.
Ethyl	1	13,770	$4·58 \times 10^2$	*iso*Propyl	1	15,890	$3·20 \times 10^3$
	2000	13,790	$2·40 \times 10^3$		2000	19,400	$2·15 \times 10^6$
	3000	13,830	$6·10 \times 10^3$		3000	20,660	$2·66 \times 10^7$
	4000	13,980	$1·61 \times 10^4$		3750	22,220	$4·38 \times 10^8$
n-Propyl	1	13,550	$4·10 \times 10^2$	*iso*Butyl	1	16,480	$4·84 \times 10^4$
	2000	13,910	$2·98 \times 10^3$		2000	17,850	$1·30 \times 10^6$
	3000	14,190	$8·87 \times 10^3$		3000	18,240	$3·35 \times 10^6$
	3750	14,740	$3·33 \times 10^4$		3750	18,780	$1·16 \times 10^7$
n-Butyl	1	13,720	$5·69 \times 10^2$	*sec.*-Butyl	1	17,460	$2·50 \times 10^4$
	2000	14,580	$7·00 \times 10^3$		2000	19,790	$3·53 \times 10^6$
	3000	14,950	$2·44 \times 10^4$		3000	21,010	$4·90 \times 10^7$
	3750	15,190	$5·72 \times 10^4$		3750	21,720	$2·22 \times 10^8$

DISCUSSION.

If the constant A be identified with the product of the collision number, Z, and a probability factor, P, then, provided the value of the former be known with some degree of certainty at the various pressures, we can obtain, through the latter, a measure of the collision efficiency and the effect of pressure thereon. There is much evidence to suggest that the frequency of binary collisions in the liquid phase is greater than in the gas phase; for instance, Evans and Polanyi (*Trans. Faraday Soc.*, 1936, **32**, 1350) relate the two frequencies through the entropies of solution of the reactants and the transition state and find log $Z_{\text{sol.}}/Z_{\text{gas}} \sim 3$ to 2; the value of Z calculated from the diffusion coefficient and the " free space " of the liquid according to Jowett's hypothesis (*Phil. Mag.*, 1929, **8**, 1059) is 10^{14}; and a value of the same order is given by Bradley's equation (*Trans. Faraday Soc.*, 1937, **33**, 1185), which is also based upon the diffusion coefficient.

FIG. 2.



We may therefore assume that the collision frequency in the liquid phase is about 10^3 times that in the gas phase under comparable conditions. If we follow Jowett's derivation, the effect of increased hydrostatic pressure will be to increase Z approximately in proportion to the increase of viscosity of the medium. In the case of reactions occurring in dilute solutions, the viscosity of the solvent only will be concerned; in our experiments, on the other hand, it is the viscosity of the reactants that matters, and unfortunately no data are available for the pressure coefficients of viscosity of the mixtures concerned. For pure liquids the coefficient varies considerably even amongst related compounds, as may be seen from the following values for a series of alcohols :

Pressure Coefficient of Viscosity (η_p/η_1) *for Alcohols at* 75° (*Bridgman*).

Substance.		EtOH.	PrOH.	BuOH.	Pr$^{\beta}$OH.	Bu$^{\beta}$OH.
p, kg./cm.^{2}	1000	1·65	1·92	2·11	2·22	2·40
	2000	2·44	3·00	3·50	3·83	4·30
	4000	4·29	5·89	7·30	8·39	11·00

If we adopt the value $\eta_{3750}/\eta_1 = 10$ for all the mixtures, then it follows from the data in Table II that at atmospheric pressure the probability factor for the *n*-primary alcohols is approximately 10^{-12} and for the *iso*- and *sec.*-alcohols is between 10^{-11} and 10^{-10}; at 3750 atm. it has increased by a factor of 10 for the former and by 10^3—10^4 for the latter. Comparing these values with the corresponding figures for typical "normal" and "slow" reactions in dilute solution (Williams, Perrin, and Gibson, *loc. cit.*), we note that whilst for most "normal" reactions the probability factor is about 1 and does not appreciably alter with pressure, yet for "slow" reactions it is of the order of 10^{-6} and the variation with pressure may be comparatively large and may be either positive or negative in sign. The data given below for the esterification of acetic anhydride with ethyl alcohol (1) in solution in large excess of the alcohol, and (2) in solution in toluene, serve to show the order of the effect:

Values of the Constant $P \times 10^6$ *for the Rate of Esterification of Acetic Anhydride with Ethyl Alcohol.*

Pressure, kg./cm.².	(1) In ethyl-alcoholic soln.	(2) In toluene soln.
1	38·5	1·3
3000	0·677	8·5

It is evident that the efficiency of collisions between reactant molecules is increased by the presence of a solvent, or conversely, that a molecule has a greater chance of losing its energy of activation by collision with other reactant molecules than by collision with solvent molecules.

The Effect of Pressure upon the E *Term of the Arrhenius Equation.*—It seems very improbable that the true activation energy of a bimolecular reaction will increase with pressure to anything like the extent that E is found to increase; E is, in fact, a composite term made up of various energy contributions, some of which are due to changes in the physical properties of the medium, and are, therefore, dependent on the pressure. Of these mention may be made of the activation energy of diffusion (Rabinowitch, *Trans. Faraday Soc.*, 1937, **33**, 1225; Bradley, *loc. cit.*), the increase of the activation energy due to the positive temperature coefficient of the collision rate (or viscosity), and the energy associated with any change in volume accompanying the formation of activated or transition complexes (Moelwyn-Hughes, *Trans. Faraday Soc.*, 1936, **32**, 1725; Evans and Polanyi, *ibid.*, 1937, **33**, 448). Unfortunately, the data required for the calculation of the value of these contributions are seldom available, and only in a few instances is it possible to obtain some idea of their relative magnitudes.

From measurements of the diffusion velocity of hydrogen peroxide in water (Stern, *Ber.*, 1933, **66**, 547), and from other considerations, it is probable that the activation energy of diffusion of liquids of the type of aliphatic alcohols and acids is of the order of 3000 cals. It has also been found that for a large number of liquids, the increase of activation energy due to the change in viscosity, as the temperature is raised, is 1500—3000 cals.

Attention may also be directed to the difference in the activation energies calculated from the temperature coefficients of the velocity constants as measured severally at constant volume and at constant pressure. The two coefficients are related by the expression

$$\left(\frac{\partial \log k}{\partial T}\right)_v = \left(\frac{\partial \log k}{\partial T}\right)_p + \left(\frac{\partial \log k}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial p}\right)_p$$

and it has been shown (Evans and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 875) that over a pressure range of 3000 atm. the difference may amount to upwards of 10%.

The energy associated with the formation of an activated or transition complex is more difficult to determine. Moelwyn-Hughes (*loc. cit.*), for example, deduces the following expression for the velocity constant, on the assumption that the reaction velocity is proportional to the number of molecules (or complexes) for which the free energy, F, has reached a certain critical value:

$$k = \text{constant} \times e^{-\Delta F^*/RT}$$

where

$$\Delta F = \Delta E + P\,\Delta V - T\,\Delta S$$

Evans and Polanyi (*loc. cit.*), also by means of a semi-thermodynamical treatment, show that the change in the velocity constant with pressure may be calculated from the equation

$$\partial \log_e k/\partial \pi = (V_1 - V_t)/\boldsymbol{R}T$$

where V_t is the molar volume of the transition state. The change in the activation energy with pressure is then given by

$$E_a = E_0 + \pi(V_1 - V_t)\{1 - T[\partial \log_e (V_1 - V_t)/\partial T]_\pi\}$$

where E_0 is the value of E_a for $\pi = 0$. From our results the values of $(V_1 - V_t)$ have been calculated and are tabulated below.

Values of $(\mathrm{V}_1 - \mathrm{V}_t)$, *c.c.*

Alcohol.	Temp. 50°.	60°.	70°.	75°.	80°.
Ethyl	21·5	22·45	22·48	23·35	—
n-Propyl	—	—	19·70	20·03	20·39
n-Butyl	—	—	18·44	18·94	19·50
*iso*Propyl	—	—	18·90	20·45	21·47
*iso*Butyl	—	—	13·70	14·23	14·84
sec.-Butyl	—	—	22·20	22·00	24·40

On plotting log k_p/k_0 against pressure, a series of nearly straight lines (Fig. 3) is obtained, indicating that for the pressure range 1—4000 atm. the volume change $(V_1 - V_t)$ is substantially independent of the pressure. Our results, however, do not enable us to calculate the variation of this quantity with temperature at constant pressure, and hence E_0 cannot be evaluated.

FIG. 3.

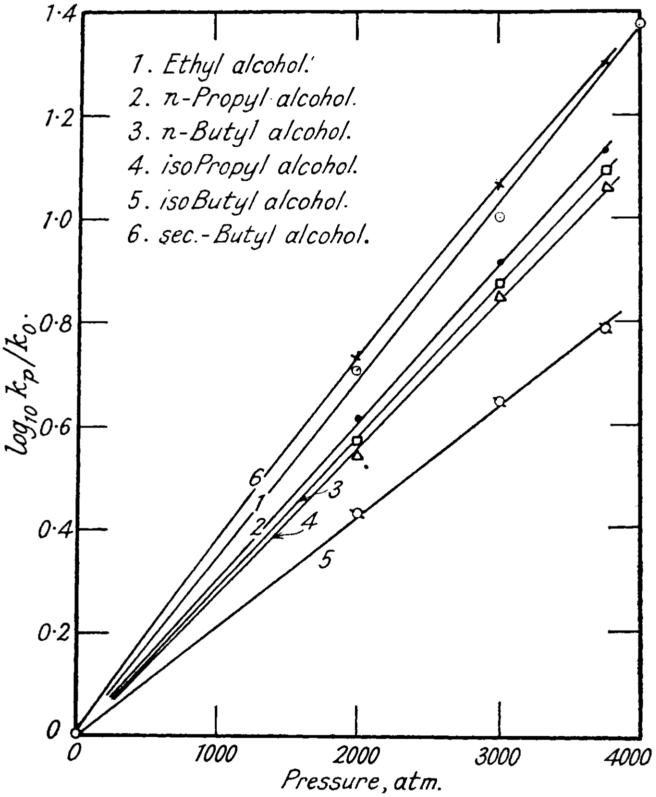
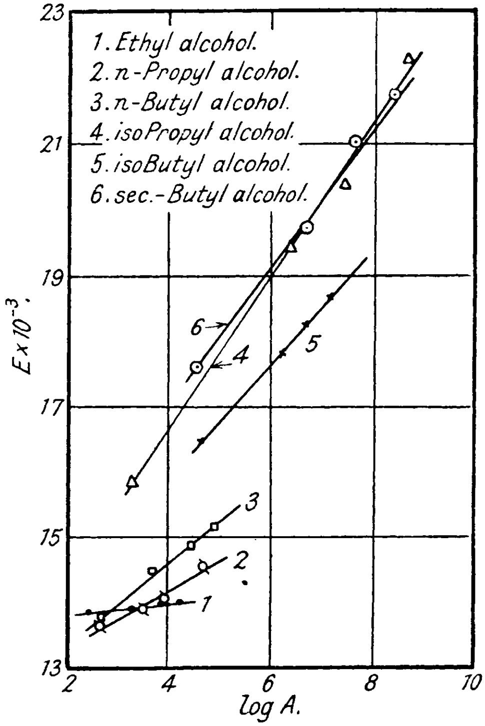


FIG. 4.



The Functional Relationship between A *and* E.—Since both A and E contain terms which are functions of pressure, we should expect a simple relationship to exist between the values of log A and E, calculated from the reaction-velocity constants determined over a range of pressures for any given reaction. That such is the case may be seen from Fig. 4, in which a linear relationship is found to hold for all the reactions.

A similar correlation of A and E has been observed for reactions in which the pressure is maintained constant but the solvent is altered; and Fairclough and Hinshelwood (J., 1937, 538) have shown that it should hold for all reactions in which the lifetime of the activated complex (the formation of which is a prelude to reaction) is less than the time taken for the internal vibrations of the molecules to attain the right phase for reaction; their theoretical treatment indicates that log A should be proportional to $1/\sqrt{E}$.

IMPERIAL COLLEGE OF SCIENCE, LONDON, S.W. 7. [*Received, April 9th,* 1938.]