(more positive at higher concentrations) and are independent of the type or charge of the cation. The rate of the electron transfer does not therefore vary significantly with the type and charge of the cation. The findings are in contrast to the observations in the reduction of the nitrate ion,[16] whose reduction potential depends strongly on the charge of the cations present.

On the other hand, the kinetic limiting current is a measure for the rate of the formation of the activated bridge complex. "Adsorption" processes such as movement of the inert cations into the Helmholtz layer are probably involved in the formation of the bridge complex and it does not seem unreasonable that the over-all rate of formation is slow. The assumption that the mercury surface is involved in the rate-determining chemical step is partially supported by the great ease with which this limiting current is suppressed by surface active material.

The rate of formation of the bridge complex increases with decreasing size and increasing charge of the hydrated cation involved. Sheppard and Wahl[14] found a similar order in the effect of inert cations on the electron exchange rate in the manganate–permanganate system.

Effect of Cations on the Reduction of Other Anions.—With the lead EDTA complex, a similar cation effect was found, but not further investigated, because of the ill-defined shape of the polarograms. Pecsok[17] reports that the wave of molybdenum(VI)–EDTA increases with electrolyte concentration and attributes the effect to the change in ionic strength. The effect is of similar order of magnitude as the one observed in the case of the CdY^{--}. By analogy, the cation effects observed with the lead and molybdenum EDTA complexes also may be the result of the formation of an ion pair or an activated bridge complex.

Minima appearing in the polarographic reduction waves of certain anions, such as $S_2O_8^{--}$, are eliminated by the addition of cations.[18,19] The effectiveness of the cations increases with their charge. Alkali ions are increasingly effective in the order Li < Na < K < Pb < Cs. Frumkin[18,19] attributed these minima to a retarded electron discharge in the potential region of the minima. The presence of cations was believed to cause changes in the structure of the double layer in such a way that the electron transfer is reaccelerated. The effect of cations on the reduction waves of this and other complex anions, such as NO_3^{-},[16] $Cd(CN)_4^{--}$,[20,22] $Hg(CN)_4^{--}$[21] can be explained by a slow formation of an activated bridge complex $Hg.^{\delta-}\ldots M^{+n}\ldots X^{-m}$ rather than by electron transfer rates only. Actually, an application of Frumkin's formula for electron transfer rates was in many cases not in concordance with the experimental results.[18,22]

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY]

Kinetic Study of Aromatic Nucleophilic Substitution under High Pressure: Bromoquinolines and Bromonaphthalenes

BY K. R. BROWER

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The displacement reactions of bromoquinolines and bromonaphthalenes with piperidine are accelerated several-fold by hydrostatic pressures up to 1300 atm. The volume changes of activation decrease throughout the sequence of increasing reactivities in accordance with the view that the faster reactions involve transition states more nearly resembling the separate reactants. Comparison of systems studied at different temperatures is justified by the absence of any measurable effect of pressure on the activation energies.

Introduction

The effect of pressure on the rates of homogeneous liquid-phase reactions has been given a theoretical explanation by Stearn and Eyring,[1] who derived from the Absolute Reaction Rate Theory the equation

$$RT(\partial \ln k/dP)_T = -\Delta V^{\pm} \qquad (1)$$

in which k is the reaction rate constant and $V^{\pm}$ is the change in molar volume resulting from the transformation of the reactant or reactants into activated complex. The volume changes of activation calculated from kinetic data on bimolecular reactions were found to be consistent with values estimated from equation 2

$$-\Delta V^{\pm} = \frac{1\text{ Å.} \times \Sigma V}{\sum\limits_i l_i + \sum\limits_i r_i + 2\text{ Å.}} \qquad (2)$$

in which ΣV is the sum of the molar volumes of the reactants, l_i is the component of length of the ith bond along the reaction coördinate, and r_1 and r_2 are the covalent radii of the terminal atoms. It is assumed that the average separation of reactant molecules is reduced by 1 Å. as the activated complex is formed. In recent years it has been found

[1] A. E. Stearn and H. Eyring, *Chem. Revs.*, **29**, 509 (1941).

that the simple theory above neglects the sometimes profound effects of electrostriction or release of solvent accompanying changes of electrical polarization during the formation of the activated complex.[2-4] Certain first-order solvolytic reactions, for example, have negative volume changes of activation because their transition states are strongly polarized and have higher solvation energies than the neutral reactants. In consequence a simple interpretation of the volume change in terms of internal bond lengths is not possible.

Discussion

This paper reports the volume changes of activation for the reactions of 2-, 6- and 8-bromoquinoline and 1- and 2-bromonaphthalene with piperidine under pseudounimolecular conditions and is an extension of an earlier study of their rates and activation energies at low pressure.[5,6] The quinolines and naphthalenes were selected for comparison because they show a wide range of electronic effects with almost no difference in the size, shape or mass of the molecules. Since these reactions result in polar products from neutral reactants, the negative volume change of activation is ascribable partly to electrostriction of solvent and partly to the formation of a new bond. Experiments on the separation of these effects by variation of reactant charge type and solvent polarity will be undertaken in the future.

The energies and volume changes of activation are listed in Table I. Values of $-\Delta V^{\pm}$ are computed from equation 1, with the use of graphically determined values of $(\partial \ln k/\partial P)_T$. It should be noted that a plot of ln k *vs.* P is curved, and the datum used is the derivative at zero pressure (see Fig. 1). It should be noted further that $\Delta V^{\pm}$ is temperature dependent, and for the purpose of comparison values have been calculated for $T = 150°$. Fortunately, in the two cases tested, $(\partial \ln k/\partial P)_T$ was found to be practically independent of temperature, and since a given increase in temperature increases k_0 and k_p in a fixed proportion, it follows that the activation energy is nearly independent of pressure.

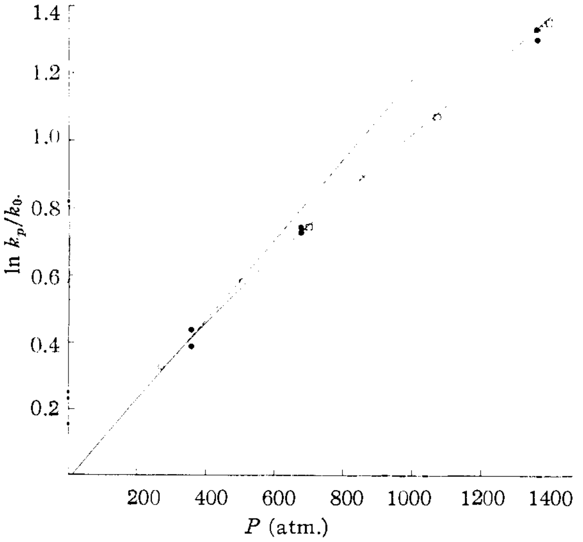


Fig. 1.—Reaction of 8-bromoquinoline with piperidine: ○, 184.3°; ●, 150.9°; □, 125.4°.

Figure 1 illustrates this behavior of 8-bromoquinoline.

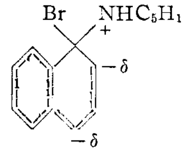
Table I

Summary of Kinetic Data

Compound	T(°C.)	$-\Delta \pm$ (150°), ml.	ΔE^{+}, kcal.	k_0 (hr.$^{-1}$)
1-Bromonaphthalene	187.8	53	25.0[a]	0.00333
2-Bromonaphthalene	189.0	63	24.9[a]	.00537
6-Bromoquinoline	184.0	64	24.4[c]	.0116
8-Bromoquinoline	125.4	41	21.0[b]	.00268
	150.9	41		.0135
	184.3	41		.0942
2-Bromoquinoline	0.0	36	12.8[c]	.0236
	27.2	36		.199

[a] Ref. 5. [b] Calculated from present data and those of T. E. Young and E. D. Amstutz, This Journal **73**, 4773 (1951). [c] Recalculated from present extension of data in ref. 6.

The interpretation of the results shown in Table I rests on the transition-state model proposed by Bunnett and Zahler.[7,8] The following structure diagrams show some of the characteristics of the proposed metastable intermediates and of the closely related activated complexes



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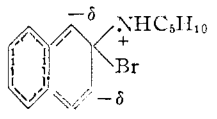

II

The high reactivity of 2-bromoquinoline can be understood by reference to II, where it is seen that the negative charge may be assumed by the nitrogen atom. Comparison of I and II suggests that 1-bromonaphthalene should be more reactive than the 2-isomer in view of the more extensive conjugation in I, but their rates and activation energies are nearly equal. Inductive activation by nitrogen causes 8-bromoquinoline to be slightly more reactive than the bromonaphthalenes, and this difference is reflected both in reaction rate and activation energy.

The volume change of activation correlates well with the theoretical predictions of relative reactivity, being highest where the reactivity is expected to be lowest. In the case of the naphthalenes it appears that the sensitivity of this parameter toward structural variation is greater than that of the activation energy. The correlation is rationalized easily with the aid of Hammond's postulate,[9] since the less endothermic activated complexes should involve less contraction along the reaction coördinate and less electrostriction of solvent, owing to the correspondingly weaker polarization.

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(3) C. T. Burris and K. J. Laidler, *ibid.*, **51**, 1497 (1955).

(4) S. D. Hamann, *Aust. J. Chem.*, **9**, 533 (1956).

(5) K. R. Brower and E. D. Amstutz, *J. Org. Chem.*, **18**, 1075 (1953).

(6) K. R. Brower, W. P. Samuels, J. W. Way and E. D. Amstutz, *ibid.*, **18**, 1648 (1953).

(7) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 297 (1951).

(8) J. F. Bunnett, E. W. Garbisch, Jr., and K. M. Pruitt, This Journal, **79**, 385 (1957).

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The aforementioned curvature of the ln *k vs. P* plots varies considerably from one compound to another and allows some interesting deductions concerning the relative compressibilities of the transition states. The reasoning is assisted by equation 3, in which ΣV is the sum of the molar volumes

$$(\partial \Delta V^{\pm}/\partial P)_T = \beta \Sigma V - \beta^{\pm} V^{\pm} \qquad (3)$$

of the reactants, β and $\beta^{\pm}$ are the compressibilities of the reactant mixture and activated complex, respectively, and $V^{\pm}$ is the molar volume of the activated complex. For the highly reactive compound 2-bromoquinoline, $(\partial \Delta V^{\pm}/\partial P)^T$ is almost zero and $\beta/\beta^{\pm} = V^{\pm}/\Sigma V$. Since the right-hand term is nearly unity, the compressibilities of the reactant mixture and activated complex are nearly the same. This implies that the two states are very similar, as Hammond's postulate would require. For the relatively unreactive 8-bromoquinoline, on the other hand, the average value of $(\partial \Delta V^{\pm}/\partial P)_T$ over the range 0–1000 atm. is about 10^{-5} l./atm. Substitution in (3), with the average value of β in the same range estimated roughly at 6×10^{-5} atm.$^{-1}$, gives $\beta^{\pm} \simeq 2 \times 10^{-5}$. This low compressibility of the activated complex suggests that it is a tightly knit system involving considerable electrostriction of solvent. It is also interesting to note that the curvature of Fig. 1 shows no systematic variation over a temperature range of nearly 60°. The variation of curvature with the reactivity of the compound is therefore probably not an artifact of the difference in the temperature ranges studied.

TABLE II

Compound	T(°C.)	P(atm.)	k(hr.$^{-1}$)
1-Bromonaphthalene	187.8	~20	0.00332
			.00334
		273	.00500
		410	.00609
		680	.00813
		1100	.0128
		1360	.0167
2-Bromonaphthalene	189.0	~20	.00549
			.00525
		275	.00867
		545	.0131
		955	.0196
		1360	.0295
6-Bromoquinoline	184.0	~20	.0116
			.0117
		340	.0219
		646	.0363
		1020	.0572
		1323	.0729
8-Bromoquinoline	184.3	~20	.0938
			.0946
		273	.1302
		505	.171
		852	.229
		1370	.357
			.361
	150.9	~10	0.0134
			.0140
			.0136
			.0130
		361	.0210
			.0200
		680	.0284
			.0282
		1360	.0495
			.0510
	125.4	0	.00267
			.00269
		695	.00566
		1070	.00786
		1395	.0103
2-Bromoquinoline	0.0	0	.0235
			.0237
		306	.0310
		848	.0590
		1390	.1001
			.0960
			.0972
	27.2	0	.205
			.197
			.197
		340	.272
			.281
			.268
		680	.407
		1360	.777
			.751

Experimental

Reagents.—2-Bromoquinoline was prepared by the method of Young and Amstutz.[10] Other reagents were prepared and purified as before.[5,6]

Apparatus.—The high-pressure equipment was purchased from stock of the American Instrument Co., Silver Spring, Maryland. Samples were inclosed in an open glass tube inverted over mercury contained in a larger tube, the whole being immersed in pressurizing oil inside the reaction vessel. A thermostat bath containing vegetable shortening was maintained within 0.1° of the setting temperature.

Procedure.—A 4-ml. sample of a 0.2 *M* solution of halide in piperidine was placed in the reaction vessel, brought to thermal equilibrium and pressurized (20–30 minutes required). This sample was removed and titrated at once in order to establish a blank, and subsequent reaction times were measured from the time of thermal equilibration. In the case of the low-temperature runs on 2-bromoquinoline, the equilibration time was eliminated by preadjustment of the temperature of the reaction vessel and sample vessel to the bath temperature. After a time sufficient for 10–60% reaction, the reaction vessel was quenched by immersion in water, the contents were withdrawn and the bromide ion content was measured as previously described.[5]

Errors.—The error in calibration and estimation of the emergent stem correction of the thermometer is probably 0.3–0.5°. The Bourdon gage used for measurement of pressure was calibrated against a free piston gage, and agreement within 1% was obtained. Previous experience with the method of preparation and analysis of samples[5] indicates a probable error of 2–3% in the rate constant, and the corresponding error in $\Delta V^{\pm}$ measured over the initial straight portion of the ln *k vs. P* curve is approximately 9%. Some conception of the precision of the rate measurements may be had by inspection of the smoothness of Fig. 1 and of the replications among the data in Table II.

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[10] T. E. Young and E. D. Amstutz, THIS JOURNAL, **73**, 4773 (1951).