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HALOGEN REACTIVITIES. II. KINETIC STUDY OF DISPLACEMENT REACTIONS OF BROMONAPHTHALENES WITH PIPERIDINE

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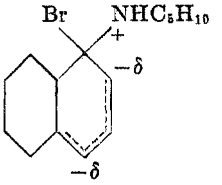
INTRODUCTION

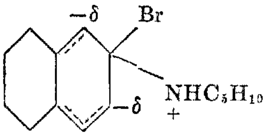
In the course of an investigation of the reactions of the haloquinolines with piperidine, it was found difficult to arrive at a reasonable explanation of their activation energies in relation to those reported for α- and β-bromonaphthalene (1). Because of the vital importance of the latter as reference points in the study of the reactivities of aromatically bound halogens, a redetermination of the activation energies was undertaken. It was also thought desirable to determine whether the reactions are actually bimolecular as is most reasonably supposed, but experimental complications, which will be more fully described, precluded that possibility.

DISCUSSION

Energies and entropies of activation for the reaction of α-, and β-bromonaphthalene with piperidine are assembled in Table II. An attempt to determine the kinetic order by carrying out the reaction in petroleum ether solution failed because the piperidine hydrobromide formed during the course of the reaction salted out part of the reactants to form a second liquid phase. It will be shown in a forthcoming publication, however, that 2-chloroquinoline reacts by a bimolecular process, and it has been assumed for the sake of computation and interpretation of the results that the reaction of the bromonaphthalenes is also bimolecular.

A consideration of the proposed structures for the transition states leads to the expectation that α-bromonaphthalene should have the lesser activation energy in view of the larger conjugated system involved. This expectation receives some support from the fact that in electrophilic substitution the greater ease of polarizability through the α-position leads mainly to α-substitution especially at low temperatures where the process having lower activation energy predominates (2). It would also be expected that α-bromonaphthalene should have the lesser entropy of activation corresponding to a more stable, more tightly bonded transition state. Such correlation between energy and entropy of activation in closely related reaction systems has often been remarked (3).





The fact that the activation energies and entropies for nucleophilic substitution at the α- and β-positions have now been found to be not appreciably different must result from compensation of the effect of unequal polarizabilities by some other factor. A possible explanation is that the *peri*-CH group produces a certain amount of steric strain in the α-activated complex, and that the strain increases the energy and also the entropy of activation by virtue of the increased bond distances and decreased bond energies and vibrational frequencies in the transition state. The nearly equal values of ΔE^* and ΔS^* observed for α- and β-bromonaphthalene might thereby be accounted for.

TABLE I

PSEUDO-UNIMOLECULAR REACTION RATES

COMPOUND	T (°C.)	k(hr.$^{-1}$)	MEAN DEVIATION
α-Bromonaphthalene	202.6	0.0068	0.0001
	217.9	.0156	.0001
	234.8	.0362	.0003
β-Bromonaphthalene	201.6	.0116	.0004
	216.8	.0246	.0010
	232.7	.0550	.0020
	241.3	.089	.003

TABLE II

COMPARISON OF RESULTS

PRESENT WORK			PREVIOUSLY REPORTED WORK (1)	
Compound	ΔE^*	ΔS^*[2]	ΔE^*[1]	ΔS^*[1, 2]
α-Bromonaphthalene	25.0 ± 0.8	−39.8 ± 1.6	24.9 ± .7	−39.7
β-Bromonaphthalene	24.9 ± 1.0	−39.0 ± 2.0	27.6 ± .7	−32.4

[1] Values for ΔS^* were not reported in the paper referred to, but have been calculated on the same basis as those reported here. Estimation of precision of Berliner's ΔE^* by the method used with present data gives an uncertainty of ±1.7 kcal.

[2] The entropies of activation were calculated by means of the equation:

$$k = (kT/h)e^{\Delta S^*/R}e^{-\Delta E^*/RT}$$

The pseudo-unimolecular rate constants were converted to second order rate constants by dividing by the concentration of piperidine before substituting in the equation. Since k has now the dimensions of liters per mole per second, the value of the thermodynamic function, ΔS^*, is based on a standard state of unit molarity.

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EXPERIMENTAL

Preparation of reagents. Technical grades of piperidine kindly contributed by the Monsanto Chemical Co., E. I. Dupont de Nemours and Co., and Hooker Electrochemical

Co. were freed from water and pyridine by refluxing over sodium for six hours and distilling. α-Bromonaphthalene, m.p. 4–6°, and β-bromonaphthalene, m.p. 56–57°, were purified by distillation in a vacuum.

Pseudo-unimolecular rate determination procedure. A 0.2 *M* solution of bromonaphthalene in piperidine was divided into 4-ml. portions which were sealed in heavy-walled glass tubes and immersed in an oil-filled thermostat bath maintained at constant temperature within ± 0.2°. Samples were removed at intervals and added to 20–30 ml. of water from which the organic material was extracted with ether. The ether extract was washed with water, and the combined aqueous layers were acidified, and the halide ion titrated potentiometrically with 0.025 *N* silver nitrate solution. The result of a typical determination is as follows:

α-Bromonaphthalene, T = 202.6 ± 0.3°C.

TIME (hr.)	(FRACTION UNREACTED)$^{-1}$	k (hr.$^{-1}$)
0	1.005	—
10	1.069	0.00697
12	1.086	.00641
14	1.105	.00677
15	1.111	.00669
16	1.118	.00668
16.5	1.123	.00673
17.0	1.131	.00695
17.5	1.132	.00681
17.5	1.132	.00681

k (av.) = 0.00676, mean Dev. = 0.00012.

Attempted determination of kinetic order. A solution 1.0 *M* in bromonaphthalene and 2.0 *M* in piperidine in purified petroleum ether, b.p. 95–100°, was divided into 5-ml. portions which were sealed in heavy-walled glass tubes and immersed in the constant temperature oil-bath at 220°. On removing the first of the tubes after ten hours it was seen that a separate liquid phase had formed rather than the expected crystalline precipitate of piperidine hydrobromide. This phase probably consisted mainly of piperidine hydrobromide dissolved in piperidine together with small amounts of bromonaphthalene and petroleum ether.

Estimation of precision of activation energies. A graphical representation of the experimental results together with those reported by Berliner (1) is given in Figure 1. The plotted points have been enlarged into rectangles of which the boundaries represent the limits of precision in measurement of rate constants and temperatures. The limits of precision of the measurement and constancy of temperature were taken as ± 0.3° which is 0.1° greater than the observed variation. This was thought to be justified inasmuch as the thermometer had been calibrated by the Bureau of Standards and the ice-point was checked several times. The limits of precision of k were taken as the mean deviation of values of k determined at a given temperature. The limits of precision of ΔE^* were then determined by drawing the two extreme slopes just cutting the first and last rectangles on the plot of log k *vs* 1/T.

It may be seen that the two sets of data do not agree as well as might be expected and it is suggested that the present data lead to considerably more precise activation energies in view of the improved temperature control (± 0.3° as opposed to 1.0°) and the greater number of rates measured. It should be pointed out that for both compounds it is possible to draw slopes of d *log* k/d (1/T) which touch all of our points as well as those of Berliner which were measured at 165°C. (1/T = 0.002281) whereas Berliner's 200° rates are badly out of agreement.

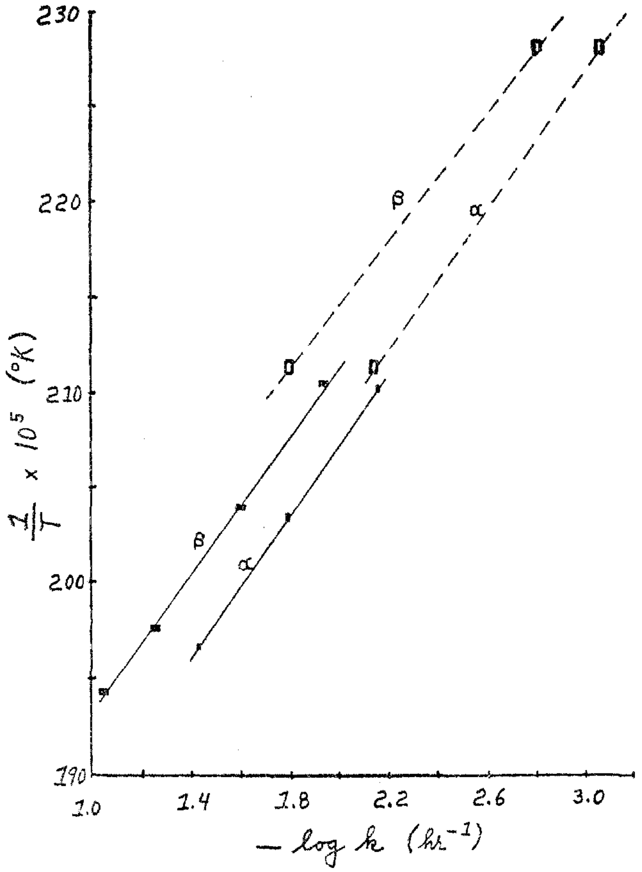

FIGURE 1. PLOT OF log k *vs* 1/T FOR α- AND β-BROMONAPHTHALENES. ---------- Previously reported work (1); ———— Present work.

SUMMARY

The reaction rates at various temperatures and the activation energies for the reaction of the bromonaphthalenes with piperidine have been redetermined and compared with the reported values. It has now been found that the difference in activation energy is negligibly small, the values for α and β being 25.0 and 24.9 kcal. respectively. The results are discussed from the standpoint of structural theory.

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