[Contribution from the Wm. H. Chandler Chemistry Laboratory, Lehigh University]

# Halogen Reactivities. VII. Kinetic Study of Displacement Reactions of Benzene, Naphthalene, and Anthracene Halides with Piperidine

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Kinetic studies on halogen replacement in the aromatic series with piperidine reveal that the addition of a benzo- or a naphtho- group has slight effect on the activation energy but brings about an appreciable increase in rate of reaction. The effect of addition of two benzo- groups has considerable effect on both rate and activation energy.

Kinetic studies of the displacement reactions of bromo-naphthalenes with piperidine[1,2] show that the 1- and 2-positions are very similar in reactivity. From this it may be inferred that in the transition state the polarizability of the ring is of much lesser importance than it is in the case of electrophilic substitution. We have thought it of interest to explore this further and the present paper reports rate studies on chloro- and bromo-benzene, 1- and 2-chloronaphthalene, 1-, 2-, and 9-chloroanthracene, and 9-bromoanthracene. In every case piperidine has been employed as the nucleophilic displacement reactant in procedures which followed closely those reported earlier.[2]

## EXPERIMENTAL

*Preparation of reagents.* Technical grade piperidine, furnished by the Hooker Electrochemical Company was freed from water and pyridine by refluxing over sodium for eight hours and distilling at 105.0–105.5°. Bromobenzene, and chlorobenzene were purified by a ordinary distillation. 1-Bromonaphthalene, m.p. 4–6°, and 2-bromonaphthalene m.p. 56–57°, were purified by vacuum distillation. 1-Chloronaphthalene was purified by ordinary distillation while 2-chloronaphthalene was prepared by a Sandmeyer reaction on 2-aminonaphthalene followed by recrystallizations from 50% ethyl alcohol, m.p. 56.8–57.4°. 1-Chloroanthracene and 2-chloroanthracene were prepared by a zinc and ammonia reduction[3] of the corresponding chloroanthraquinones. 1-Chloroanthracene was recrystallized from acetic acid, m.p. 80.5–81.5°. The reported m.p. is 81–82°.[4] 2-Chloroanthracene was recrystallized from glacial acetic acid, m.p. 215–217°. The reported m.p. is 215°.[5] 9-Bromoanthracene was prepared by direct bromination of anthracene in $CCl_4$ followed by recrystallization from ethyl alcohol,[6] m.p. 100–101°. The reported m.p. is 100–101°.[6] 9-Chloroanthracene was prepared in poor yield by direct chlorination of anthracene in $CS_2$, followed by recrystallization from ethyl alcohol,[7] m.p. 106–108°. The reported m.p. is 103°.[7]

*Pseudounimolecular rate procedure.* A 0.2 $M$ solution of the halide in piperidine (excepting 2-chloroanthracene, which, because of slight solubility, had to be run at 0.05 $M$) was divided into 4-ml. portions which were sealed in heavy-walled Pyrex glass. These tubes were placed in a constant temperature bath, (boiling tetralin for temperatures of 207–210° and Spry[8] for temperatures greater than 210°) and removed at constant intervals. The contents were dissolved in acetone, made acid with 7 $N$ $HNO_3$, and titrated with 0.025 $N$ $AgNO_3$. For the titration, a 5-ml. micro-buret with micro-tip was used with a silver electrode and a calomel electrode containing saturated $K_2SO_4$ solution rather than KCl.

*Determination of reaction products.* To ascertain that the configuration of the products of reaction corresponded to that of the starting material, each reaction was run on a larger scale and isolation of the products was attempted. In every case, save those of the derivatives of 1- and 2-anthracene, the products appeared to be made up only of the known piperidino derivatives.[9]

*2-Piperidinoanthracene* was isolated as a brilliant yellow solid which melted at 162–164° after recrystallization from 95% ethanol.

*Anal.* Calc'd for $C_{19}H_{19}N$: C, 87.36; H, 7.28; N, 5.36. Found: C, 87.30; H, 7.21; N, 5.36.

Its *picrate* melted at 113–115°. Its ultraviolet absorption spectrum possessed peaks at 3200 A°, 3370 A°, 3550 A°, and 4100 A°. The known 2-aminoanthracene spectrum has peaks at 3180 A°, 3340 A°, 3520 A°, and 4100 A°.

*1-Piperidinoanthracene* could not be isolated in pure condition because of rapid air oxidation. It thus appears to be quite different from the 2-isomer. It does not seem likely that cine-substitution has occurred here but the point has not been rigorously proved yet.

## DISCUSSION

Because of the marked similarities of the activation energies of the phenyl and naphthyl halides it may be concluded either that the benzopentadienate ion has only slightly greater stability than the bare pentadienate ion or that there is no parallelism between the free energies of formation of the activated complexes and the corresponding pentadienate "intermediates." The latter case might result if the nucleus is not appreciably polarized in the activated complex, the energy of activation being identified with the repulsion energy between the unshared electron pair of the nucleophilic reagent and the *pi*-electron cloud of the nucleus.

When the halogen occupies the 9-position of an-

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(1) Berliner, Quinn, and Edgerton, *J. Am. Chem. Soc.*, **72**, 5305 (1950).

(2) Brower and Amstutz, *J. Org. Chem.*, **18**, 1075 (1953).

(3) Liebermann, *Ann.*, **212**, 57 (1883).

(4) Fischer and Ziegler, *J. prakt. Chem.*, **86**, 293 (1912).

(5) Schilling, *Ber.*, **46**, 1068 (1913).

(6) Bachmann and Kloetzel, *J. Org. Chem.*, **3**, 58 (1938).

(7) Perkin, *Chem. News*, **34**, 145 (1876).

(8) A hydrogenated vegetable oil.

(9) Bunnett and Brotherton, *J. Am. Chem. Soc.*, **78**, 155 (1956) have conclusively demonstrated that ciné-substitution is not involved in the reactions of 1- and 2-bromonaphthalenes with piperidine.

TABLE I
RATE STUDIES OF HALOGEN DISPLACEMENT IN AROMATIC COMPOUNDS

| Compound | $T_{Corr}$, °C. | k (hrs.$^{-1}$) | $\Delta$ E* (kcal/mole) | log pZ |
|---|---|---|---|---|
| Bromobenzene | 193.0 | 0.00263 ± 0.00006 | 24.1 ± 0.4 | 7.73 ± 0.19 |
| | 232.5 | 0.0198 ± 0.0002 | | |
| | 240.5 | 0.0292 ± 0.0006 | | |
| Chlorobenzene | 209.0 | 0.0003799 ± 0.0000115 | 26.8 ± 1.4 | 7.71 ± 0.62 |
| | 234.1 | 0.001505 ± 0.000017 | | |
| | 257.0 | 0.00482 ± 0.00050 | | |
| 1-Bromonaphthalene[2] | 202.6 | 0.0068 ± 0.0001 | 25.0 ± 0.35 | 8.21 ± 0.16 |
| | 217.9 | 0.0156 ± 0.0001 | | |
| | 234.8 | 0.0362 ± 0.0003 | | |
| 2-Bromonaphthalene[2] | 201.6 | 0.0116 ± 0.0004 | 25.0 ± 0.84 | 8.52 ± 0.38 |
| | 216.8 | 0.0246 ± 0.0010 | | |
| | 232.7 | 0.0550 ± 0.0020 | | |
| | 241.3 | 0.089 ± 0.003 | | |
| 1-Chloronaphthalene | 210.4 | 0.001753 ± 0.000044 | 25.4 ± 1.0 | 7.74 ± 0.45 |
| | 234.1 | 0.006676 ± 0.000207 | | |
| | 254.1 | 0.01578 ± 0.00100 | | |
| 2-Chloronaphthalene | 208.0 | 0.001556 ± 0.000032 | 23.1 ± 0.5 | 6.67 ± 0.22 |
| | 231.2 | 0.00474 ± 0.00013 | | |
| | 233.5 | 0.00501 ± 0.00022 | | |
| | 255.7 | 0.01368 ± 0.00035 | | |
| 1-Chloroanthracene | 207.8 | 0.001189 ± 0.000091 | 23.8 ± 1.7 | 6.85 ± 0.76 |
| | 233.3 | 0.003705 ± 0.000119 | | |
| | 251.6 | 0.00957 ± 0.00070 | | |
| 2-Chloroanthracene | 208.0 | 0.002952 ± 0.000408 | 26.5 ± 2.0 | 8.48 ± 0.91 |
| | 234.1 | 0.01235 ± 0.00061 | | |
| | 253.9 | 0.03268 ± 0.00163 | | |
| 9-Chloroanthracene | 208.4 | 0.0218 ± 0.0011 | 20.1 ± 1.1 | 4.73 ± 0.78 |
| | 235.1 | 0.0600 ± 0.0039 | | |
| | 250.5 | 0.1170 ± 0.0046 | | |
| 9-Bromoanthracene | 185.4 | 0.0389 ± 0.0008 | 16.0 ± 0.6 | 6.36 ± 0.49 |
| | 199.4 | 0.0625 ± 0.0010 | | |
| | 211.6 | 0.1010 ± 0.0010 | | |
| | 222.1 | 0.143 ± 0.004 | | |

thracene there is a significant increase in the rate of its removal and an equally significant lowering of the activation energy. We suggest that the cumulative effect of the two benzo groups lowers the free energy of formation of the "metastable intermediate" to such a degree that the activated complex begins to resemble it in being somewhat polarized. At the same time it must be admitted than an "anthracyne" type intermediate, even though it is very improbable is not ruled out.[10] It is planned that a future communication will deal with this.

Our present view, which coincides with that of Bunnett and Zahler,[11] is that pentadienate anion resonance is insufficient to confer much stability on the reaction intermediate which therefore greatly resembles the transition state. This resemblance gradually fades as one and two benzo groups are fused on.

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BETHLEHEM, PENNSYLVANIA

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(10) 9-Chloroanthracene is reported to give 9-piperidinoanthracene but is not known whether the 9-position of the product is also the 9-position of the starting material. Lellmann and Gellner, *Ber.*, **21**, 2279 (1888).

(11) Bunnett and Zahler, *Chem. Revs.*, **49**, 273 (1951).