

**Preparation of Solutions.**—Reproducible kinetic data were obtained only when moisture was very carefully excluded. All solutions were prepared in a dry-box in the presence of phosphorus pentoxide. Solutions of ferric chloride prepared in this way and stored in flasks wrapped in aluminum foil to exclude light showed no change in activity after 10 to 14 days. Glassware was dried in an oven at 110° and then transferred to the dry-box where it was allowed to cool. The reaction cells used for kinetic runs were filled in the dry-box and immediately transferred to the apparatus previously described.<sup>15</sup>

**Determination of Acetone.**—The reaction vessel was fitted with a serum stopper and samples were withdrawn periodically by means of a syringe. The samples were transferred to cooled glass vials which were also sealed with serum stoppers. Samples

were examined by vapor chromatography on a Carbowax column at 55°. Amounts were estimated by comparison of the areas of the elution peaks in comparison with the peak areas given by standard solutions of acetone in chlorobenzene-cumene. After 3,000 seconds, shortly before the end of the inhibition period, the acetone concentration had risen to  $6.7 \times 10^{-3} M$ . During this time  $14.2 \times 10^{-3}$  mole/liter of oxygen had been absorbed and  $9.4 \times 10^{-3}$  mole/liter of radicals had been produced. Analyses after 17,000 and 25,000 seconds indicated acetone concentrations of  $5.8 \times 10^{-3}$  and  $6.3 \times 10^{-3} M$ , respectively.

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## The Basic Strengths of Some Aromatic Aldehydes and Ketones

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The  $pK_{BH}^+$  values of ten aromatic carbonyl compounds have been determined. The variations of basic strengths within the series of aromatic aldehydes agree with theoretical predictions based on molecular orbital theory. The discrepancies noted for other aromatic carbonyls are discussed.

Although aromatic aldehydes and ketones are usually regarded as very weak bases, various stable salts of several members of this class of compounds have nonetheless been known for a long time. For example, the perchlorate salts of benzalacetophenone, dibenzalacetone and benzophenone were reported early this century.<sup>1</sup>

It is significant that only salts of the more highly conjugated members appear to be stable enough to allow isolation. There do not appear to be any reports of the isolation of salts of benzaldehyde or acetophenone, for example. The explanation of this apparent significant difference in basic strength appeared then to present an interesting problem and prompted the present investigation. Very little quantitative data on the basic strengths of aromatic aldehydes and ketones were available from the literature and this paper reports these data for some ten such compounds and describes attempts to correlate the observed basic strengths with molecular structure.

### Results and Discussion

The basic strengths of the compounds listed in Table I were determined spectrophotometrically in aqueous sulfuric acid solutions using the method reported by Hammett and co-workers<sup>2</sup> for determination of basic strengths of weak bases.

TABLE I  
THE  $pK_{BH}^+$  VALUES FOR VARIOUS AROMATIC CARBONYL COMPOUNDS

Number	Compound	$pK_{BH}^+$	$\sigma_{or}^2$
1	Benzaldehyde	-6.99	0.571
2	2-Naphthaldehyde	-6.68	.529
3	9-Phenanthraldehyde	-6.39	.446
4	1-Naphthaldehyde	-6.34	.450
5	1-Anthraldehyde	-5.71	.381
6	9-Anthraldehyde	-4.81	.286
7	Acetophenone	-6.04 <sup>a</sup>	.571
8	2-Acetylnaphthalene	-6.04	.529
9	1-Acetylnaphthalene	-5.86	.450
10	1-Acetylanthracene	-5.65	.381
11	Perinaphthenone	-1.40	.167

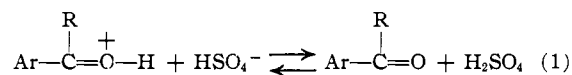
<sup>a</sup> Previously reported by Hammett and co-workers.<sup>2</sup>

(1) (a) K. A. Hofmann, *Ber.*, **42**, 4857 (1909); **43**, 178 (1910); (b) P. Pfeiffer, *Ann.*, **412**, 253 (1916).

(2) L. A. Flexser, L. P. Hammett and A. Dingwall, *J. Am. Chem. Soc.*, **57**, 2103 (1935).

With the notable exception of perinaphthenone, the compounds listed vary in basic strengths by a little more than two  $pK$  units. 9-Anthraldehyde is the most basic aldehyde of the series; we find it readily forms a red perchlorate salt when treated with perchloric acid.

In any explanation of the variations of  $pK_{BH}^+$  shown in Table I it seems safe to assume that salt formation with each base involves protonation of the carbonyl oxygen and that the equilibrium reaction involved is as shown in eq. 1.



Consider first the aromatic aldehydes. The base and the conjugate acid for each carbonyl compound both possess the same number of  $\pi$ -electrons; hence, unlike variations in basic strengths of arylamines or aromatic hydrocarbons, the variations of  $pK_{BH}^+$  values cannot be attributed to changes in  $\pi$ -electron localization energies. Furthermore, of the various factors contributing to the total free energy changes involved in eq. 1, changes in O-H bond energy and changes in solvation energies are not expected to vary significantly from one carbonyl system to another. The one factor which is not expected to remain constant, and which is therefore considered mainly responsible for the variations in the basic strengths, is the change in total  $\pi$ -electron energy when the effective electronegativity of oxygen is changed following protonation. If this change in total  $\pi$ -electron energy of the system is denoted by  $\Delta E_\pi$  then it follows that a linear relationship such as eq. 2 should exist between the  $\Delta E_\pi$  and the  $pK_{BH}^+$  values for the various aldehydes.

$$\Delta E_\pi = a + b \times pK_{BH}^+ \quad (2)$$

Attempts to correlate the data in Table I then require determination of  $\Delta E_\pi$ . One obvious way this could be done would be to calculate separately, for each molecule, the total  $\pi$ -energy of the protonated and unprotonated species using the Hückel molecular orbital method. However, this approach would require some guess made as to the electronegativity parameters appropriate for oxygen and protonated oxygen. Also the method would involve considerable computation. Instead we have made use of a perturbation method

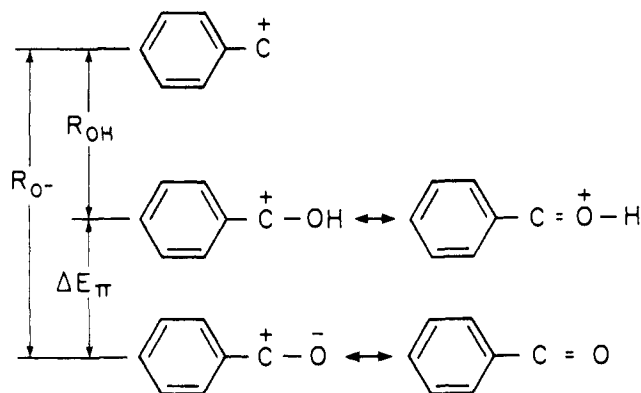


Fig. 1.—Energy levels of the benzyl cation, benzaldehyde and protonated benzaldehyde.

already outlined in a general form by Dewar<sup>3</sup> in a series of papers dealing with the application of perturbation methods in general to problems in organic chemistry. Theorem 41 in this series states, in effect, that attachment of a +E substituent, possessing two  $p_z$ -electrons, to a carbonium ion containing an odd number of carbon atoms (and possessing no odd membered rings) will, to a first approximation, stabilize the system by an amount  $R$ , where

$$R = -2a_{or}^2\beta^2/\alpha \quad (3)$$

In 3,  $\alpha$  is the electronegativity parameter (coulomb integral) of the substituent attached to carbon atom  $r$ ,  $a_{or}$  is the coefficient of the atomic orbital of carbon atom  $r$  in the non-bonding molecular orbital and  $\beta$  is the usual resonance integral.

In the application of 3 to the present problem let us consider first the aromatic aldehydes. The  $\pi$ -electron framework of benzaldehyde may be considered as being derived from attachment of an oxygen anion to a benzyl carbonium ion. The stabilization following the attachment will be, from 3

$$R_{O^-} = -2a_{or}^2\beta^2/\alpha_{O^-} \quad (4)$$

where  $\alpha_{O^-}$  is the appropriate electronegativity parameter for an oxygen anion.

Similarly, the protonated form of benzaldehyde may be derived from attachment of a hydroxyl radical to a benzyl cation and, in this instance, the stabilization of the system will be

$$R_{OH} = -2a_{or}^2\beta^2/\alpha_{OH} \quad (5)$$

$\alpha_{OH}$  being the electronegativity parameter of oxygen in the OH group.

These energy terms are represented in Fig. 1. It follows that  $\Delta E_{\pi}$ , the difference in  $\pi$ -energy between benzaldehyde and its conjugate acid, will be

$$\Delta E_{\pi} = R_{O^-} - R_{OH} = 2a_{or}^2\beta^2(1/\alpha_{OH} - 1/\alpha_{O^-}) \quad (6)$$

Now for a series of aldehydes  $\alpha_{O^-}$  and  $\alpha_{OH}$  will remain constant; therefore, from 6 and 2 a linear relationship should exist between  $pK_{BH^+}$  and  $a_{or}^2$ . The values of  $a_{or}^2$  for the various systems are very simply calculated by the method already described by Longuet-Higgins.<sup>4</sup>

The experimental plot of  $pK_{BH^+}$  against  $a_{or}^2$  is shown in Fig. 2. The linear relationship (full line) predicted by 6 is very satisfactorily attained and the line drawn in Fig. 2 could probably be employed usefully for predictive purposes.

Application of eq. 6 to a series of aryl methyl ketones should also lead to the same linear relationship; for example, both acetophenone and benzaldehyde would be associated with the same value of  $a_{or}^2$ . Because of

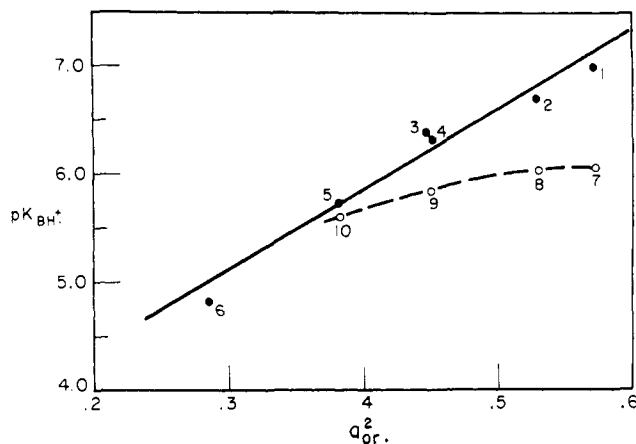


Fig. 2.—Plot of  $pK_{BH^+}$  vs.  $a_{or}^2$  for the carbonyl compounds listed in Table I.

the fairly rapid decomposition which occurs in the strong acid solutions we have not been able to measure the  $pK_{BH^+}$  values for many of these members. However for those compounds which are stable in acid (listed in Table I) it is apparent that the same relationship does not hold as was found for the aldehydes. For the less basic members the aryl methyl ketones are significantly more basic than the corresponding aldehydes, but this difference decreases with increasing basic strength (dotted line in Fig. 2). A possible explanation of this trend is seen in the inductive effect of the methyl group. For the case of acetophenone the carbon atom attached to the methyl group will bear a fairly large positive charge in the protonated species and the inductive stabilization of methyl will be large. For the more conjugated members the positive charge will be more dispersed and the inductive stabilization of the conjugate acid, relative to the free base, will become less significant.

For obvious reasons good agreement with the linear plot shown in Fig. 2 will probably not be found for other aldehyde systems, such as cinnamaldehyde, in which rotation about bonds in the conjugated system can occur. This effect would also play a part in the basicities of diaryl ketones. Even so, the  $a_{or}^2$  values for these compounds still probably has some qualitative value. Thus benzalacetophenone is a stronger base than *p*-benzoyldiphenyl in agreement with the  $a_{or}^2$  values (0.286 and 0.372, respectively); however,  $\beta$ -benzointhalene is a stronger base than the latter of these two, yet has an  $a_{or}^2$  value of 0.379. It is also of interest that the abnormally low value of  $a_{or}^2$  for perinaphthenone (I) (0.167) is in qualitative accord with the unusually basic properties of this ketone ( $pK_{BH^+} - 1.40$ ).

### Experimental

**Materials.**—The 9-phenanthraldehyde, 1- and 2-naphthaldehydes and 1- and 2-acetylnaphthalenes were obtained commercially and purified until the melting points checked with reported values. 9-Anthraldehyde was prepared by the method reported by Fieser, Hartwell and Jones.<sup>5</sup>

1-Anthraldehyde and 1-acetylanthracene were prepared as follows.

**1-Anthraldehyde.**—1-Anthracenecarboxylic acid<sup>6</sup> (10 g., 0.05 mole), thionyl chloride (55 g.) and 1 drop of pyridine were dissolved in dry benzene (50 ml.) and the mixture heated under reflux for 2 hours. After removal of the solvent under reduced pressure the mixture was extracted with hot petroleum ether. Upon cooling the extract, 1-anthracenecarboxylic acid chloride separated and was collected (8.3 g., m.p. 95–96°).

A solution of *t*-butyl alcohol (5.6 g.) in dry ether (10 ml.) was added slowly, with stirring, to a solution of lithium aluminum

(3) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3341, 3345, 3350, 3353, 3355, 3357 (1952).

(4) H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265 (1950).

(5) L. F. Fieser, J. L. Hartwell and J. E. Jones, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 98.

(6) E. de Barry Barnett, J. W. Cook and H. H. Grainger, *Ber.*, **57**, 1777 (1924).

hydride (0.86 g.) in ether (50 ml.). The ether was decanted and the residue dissolved in diglyme. The resulting solution was added dropwise to a stirred solution of the above acid chloride (5.0 g.) in dry diglyme cooled to  $-70^\circ$  in a Dry Ice-acetone-bath. The mixture was allowed to warm slowly to room temperature, then poured onto cracked ice and extracted with benzene. Removal of the benzene and recrystallization of the residue from ethanol gave 1-anthraldehyde (0.5 g., yellow needles from ethanol; m.p. 125–128°).

*Anal.* Calcd. for  $C_{15}H_{10}O$ : C, 87.30; H, 4.85. Found: C, 87.27; H, 4.71.

**1-Acetylanthracene.**—A solution of methylolithium (about 2.0 g.) in ether (150 ml.) was added to a stirred suspension of 1-anthracenecarboxylic acid in ether. After the addition, the mixture was heated under reflux for 30 minutes, then cooled and water and dilute HCl added. The ether layer was washed with  $Na_2CO_3$  solution, dried over  $MgSO_4$  and the solvent then removed. The 1-acetylanthracene (2.8 g., 56 g.) was recrystallized from ethanol; m.p. 105–108°.

*Anal.* Calcd. for  $C_{16}H_{12}O$ : C, 87.27; H, 5.45. Found: C, 87.09; H, 5.60.

The 2,4-dinitrophenylhydrazones formed orange needles from ethyl acetate; m.p. 265–267°.

*Anal.* Calcd. for  $C_{22}H_{16}O_4N_4$ : C, 65.99; H, 4.03; N, 14.00. Found: C, 65.61; H, 4.29; N, 14.23.

**Measurement of  $pK_{BH^+}$  Values.**—The procedure used is outlined in detail by Hammett and co-workers.<sup>2</sup> Weighed samples of the carbonyl compounds were dissolved in varying strength aqueous sulfuric acid solutions and the ultraviolet spectra taken on a Beckman model DB spectrophotometer. Corrections for spectral shifts due to solvent changes were made utilizing the "isosbestic point" method outlined by Hammett and co-workers. The  $pK_{BH^+}$  values were determined from the equation  $H_0 = pK_{BH^+} - \log ([R^+]/[ROH])$ , the  $H_0$  values being taken from a large scale plot of the  $H_0$  acidity function. A more detailed discussion of the method, as applied to the present series of compounds, is available elsewhere.<sup>7</sup>

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(7) Ph.D. Thesis of George S. Culbertson, Univ. of Texas, 1962.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

## Equilibria in Halogen-Lithium Interconversions

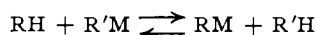
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Several halogen-lithium interchange equilibria have been measured to obtain the relative stabilities of various alkyl-, cycloalkyl-, alkenyl- and aryllithium reagents. Data and arguments are presented to show that the equilibrium constants are primarily affected by some structural parameter of the simple organolithium reagent, and it is concluded that the data may serve as a quantitative or semiquantitative measure of carbanion stability.

### Introduction

Despite the interest there would obviously be in a knowledge of relative stabilities of carbanions, surprisingly little is known about the simple hydrocarbon anions. Semiquantitative measurements of "acidity" of hydrocarbons have been carried out in a few pioneering studies,<sup>1</sup> restricted necessarily to cases where the carbanions enjoy conjugative stabilization. The equilibria studied were exchange reactions of the type

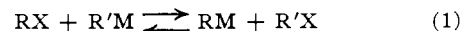


where M was sodium or potassium. Because of the non-polar media required and because of possible covalent character in the RM bonds, it was not possible to derive  $K_a$ 's which could be compared quantitatively with  $K_a$ 's of stronger acids in aqueous media, but the equilibria were of the same basic type as acid-base equilibria and were probably just as valid as the latter in establishing an order of anion stability. More recently, kinetic (rather than equilibrium) measurements of proton availability have provided promising approaches to stabilities of conjugated and acetylenic carbanions.<sup>2</sup>

(1) (a) J. B. Conant and G. W. Wheland, *J. Am. Chem. Soc.*, **54**, 1212 (1932); (b) W. K. McEwen, *ibid.*, **58**, 1124 (1936); (c) R. D. Kleene and G. W. Wheland, *ibid.*, **63**, 3321 (1941); (d) N. S. Wooding and W. C. E. Higginson, *J. Chem. Soc.*, 774 (1952).

(2) (a) D. Bryce-Smith, *ibid.*, 1079 (1954); (b) D. Bryce-Smith, V. Gold and D. P. N. Satchell, *ibid.*, 2743 (1954); (c) A. I. Shatenshtein, *Doklady Akad. Nauk S.S.S.R.*, **70**, 1029 (1950) (*C. A.*, **44**, 5194 (1950)); (d) A. I. Shatenshtein, N. M. Dykhno, E. A. Izraelievich, L. N. Vasil'eva and M. Faivush, *ibid.*, **79**, 479 (1951); (e) A. I. Shatenshtein and E. A. Izraelievich, *Zhur. Fiz. Khim.*, **32**, 2711 (1958); (f) A. I. Shatenshtein, *ibid.*, **26**, 1206 (1951); (g) A. I. Shatenshtein, L. N. Vasil'eva, N. M. Dykhno and E. A. Izraelievich, *Doklady Akad. Nauk S.S.S.R.*, **85**, 381 (1952); (h) F. S. Yabushin, U. G. Dubinskii, E. A. Yakovleva and A. I. Shatenshtein, *Zhur. Fiz. Khim.*, **33**, 2821 (1959); (i) N. M. Dykhno and A. I. Shatenshtein, *ibid.*, **28**, 11 (1954); *C. A.*, **48**, 10413d (1954); (j) H. Hart and R. E. Crocker, *J. Am. Chem. Soc.*, **82**, 418 (1960); (k) A. Streitwieser, Jr., D. E. Van Sickle and W. C. Langworthy, *ibid.*, **84**, 244 (1962); (l) A. Streitwieser, Jr. and D. E. Van Sickle, *ibid.*, **84**, 249 (1962); (m) A. Streitwieser, Jr., W. C. Langworthy and D. E. Van Sickle, *ibid.*, **84**, 251 (1962); (n) A. Streitwieser, Jr., and D. E. Van Sickle, *ibid.*, **84**, 254 (1962); (o) A. Streitwieser, Jr., D. E. Van Sickle and L. Reif, *ibid.*, **84**, 258 (1962); (p) R. E. Dessy, Y. Okuzumi and A. Chen, *ibid.*, **84**, 2899 (1962).

None of the techniques thus far described have been generally applicable to the less acidic (non-benzylic and non-allylic) hydrogens found in simple hydrocarbons. The present research was undertaken to see whether the halogen-metal interchange reaction (1) could be used to obtain quantitative data in the region of very low acidities. This reaction is formally similar to the acid-base equilibria traditionally used except



that the two bases compete for a halogen atom rather than a hydrogen atom. Examples of halogen-metal interchange are known in which the metal is sodium,<sup>3</sup> magnesium,<sup>4</sup> barium,<sup>4b</sup> aluminum<sup>4c</sup> and lithium,<sup>5</sup> but the last metal is the most generally useful. For the purpose of obtaining carbanion stabilities, it would be desirable to maximize the ionic character of the R-M bond by the use of sodium or potassium, but lithium was nevertheless chosen for our initial studies because of anticipated difficulties with solubilities and with side reactions (such as Wurtz coupling and ether cleavage) to be expected from the other alkali metal alkyls. The halogen may normally be either bromine or iodine,<sup>5</sup> and both are examined in the present work.

It is known qualitatively that halogen-lithium exchanges favor alkenyl or aryllithiums over alkyl-lithiums<sup>5</sup> and cyclopropyllithiums over alkyl-lithiums,<sup>6</sup> and it is known that exchanges involving very similar alkyl or aryl groups lead to equilibrium mixtures containing the four possible components in comparable amounts.<sup>7</sup> However, systematic, quantitative determinations of the equilibrium constants do not appear to have been attempted.

(3) H. Gilman, F. W. Moore and O. Baine, *ibid.*, **63**, 2479 (1941).

(4) (a) H. Gilman and S. M. Spatz, *ibid.*, **63**, 1553 (1941); (b) H. Gilman, A. H. Haubein, G. O'Donnell and L. A. Woods, *ibid.*, **67**, 922 (1945); (c) H. Gilman and A. H. Haubein, *ibid.*, **67**, 1033 (1945).

(5) R. G. Jones and H. Gilman, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 339.

(6) (a) H. M. Walborsky and F. J. Impastato, *J. Am. Chem. Soc.*, **81**, 5835 (1959); (b) D. E. Applequist and A. H. Peterson, *ibid.*, **83**, 862 (1961).

(7) H. Gilman and R. G. Jones, *ibid.*, **63**, 1441 (1941).