Acidities of Alkylarenes from the Equilibria of Their Sodium Salts

G. Gau* [1] **and S. Marques**

Contribution from the Centre de Cinétique Physique et Chimique
CNRS, 54600 Villers, France. *Received March 31, 1975*

Abstract: Equilibrium ion-pair acidities are reported for 18 hydrocarbons toward diamine chelated phenylsodium in hydrocarbon solvents. The equilibrium constants of the competitive equilibria are calculated from the concentrations of the methyl derivatives obtained by quenching the organosodium compounds with dimethyl sulfate. The hydrocarbons investigated have a range of acidity extending from diphenylmethane to cumene. The results are compared, by means of a Bronsted plot, to a kinetic scale of acidity deduced from hydrogen isotope exchange reactions.

The equilibrium and kinetic acidities of various low acidity hydrocarbons, such as polyarylmethanes and monoarylalkanes, have been recently compared by Streitwieser et al.[2]

The relative *equilibrium acidities* of the two hydrocarbons, R_1H and R_2H, were obtained from competitive equilibria with cesium cyclohexylamide (CsCHA) in cyclohexylamine (CHA):

$$R_1H + R_2^-Cs^+ \rightleftharpoons R_1^-Cs^+ + R_2H$$

the equilibrium constants being used to define a quantitative "ion-pair" acidity scale.

Since cyclohexylamine is more acidic than toluene, the method cannot be used to define the acidities of the monoarylalkanes. The relative acidities of the monoarylalkanes are usually evaluated from their *kinetic acidities*,[2,3] i.e., hydrogen isotope exchange reactivities toward lithium cyclohexylamide in cyclohexylamine[2] or toward potassium amide in ammonia.[3]

We wish to report on a new method to determine "ion-pair" equilibrium constants which is less limited by the acidity of the solvent since any aromatic or paraffinic hydrocarbon may be used as a reaction medium.

The two hydrocarbons to be compared, R_1H and R_2H, are caused to react in a competitive equilibrium with the complex C_6H_5Na–diamine and the equilibrium

$$R_1H + R_2^-Na^+\text{-diamine} \overset{K_{12}}{\rightleftharpoons} R_1^-Na^+\text{-diamine} + R_2H \quad (1)$$

is evaluated. R_1H and R_2H are preferentially more acidic than benzene, and in this case the complexes R_1Na–diamine and R_2Na–diamine are, in general, soluble in the hydrocarbon solvent. The hydrocarbon solvent is either an alkane or the mixture R_1H–R_2H. The diamine is a chelating *tertiary* diamine, less acidic than benzene. Other tertiary polyamine chelated alkali metal compounds[4] can also be used.

Experimental Section

Phenylsodium. A sodium dispersion is prepared in a high-boiling solvent such as decahydronaphthalene, *p*-xylene, etc. On the laboratory scale the preferred method[5] of dispersion is by ultrasonic radiation with a magnetostrictive ultrasonic transducer operating at 20 kHz. In this case, the majority of the sodium particles of the dispersion are not greater than 5 μ in diameter.

High-speed stirring techniques may also be used, and the stirrers known as "colloid mills" (Ultra Turrax T-45 commercialized by Janke and Hunkel in Germany, for example) gave satisfactory results.

The sodium dispersion is attacked by chlorobenzene[6]:

$$2Na + C_6H_5Cl \rightarrow ClNa + C_6H_5Na$$

A slight excess of sodium must always be used, and under these conditions a mixture of solid C_6H_5Na, NaCl, and Na is obtained. This phenylsodium suspension may be stored in an inert atmosphere for more than a month. Before use, the suspension is homogenized by magnetic stirring and transferred by syringe to the metalation flask (aliquots of 0.01 mol of C_6H_5Na in 10 ml, for example).

Polyamines. In this study, we refer to the following N-permethylated tertiary polyamines: *N,N,N',N'*-tetramethylethylenediamine (TMED); *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDT); *N,N,N',N'',N''',N'''*-hexamethyltriethylenetetramine (HMTT); *N,N,N',N'*-tetramethyl-1,2-diaminocyclohexane-(TMCHD).

The tetramethylethylenediamine is a Fluka product, stored over calcium hydride and used without further purification. The other amines were prepared by methylation of the parent primary amines. The 1,2-diaminocyclohexane (essentially trans) was purchased from Aldrich Chemical Co. Methylation is made via the Eschweiler–Clarke reaction with an excess of methanal and formic acid as described in a patent.[7] The N-permethylated amines were purified by vacuum distillation and analyzed by VPC on Celite 22 impregnated with potassium hydroxide and Apiezon L.

Sodium–Hydrogen Exchange Reactions. A small reactor (50 ml) swept with nitrogen is charged with the phenylsodium suspension and either with R_1H or with the R_1H–R_2H mixture. The chelating polyamine is added (1 mol of polyamine per mol of organosodium), and within a very short time the suspension exhibits the colors of the alkylaromatic anions. Phenylsodium complexed to the diamine is not soluble in the hydrocarbons as is verified by centrifugation experiments, but the alkylaromatic complexes are soluble, and in many cases their solubilities are higher than 1 mol/l.

Since no effect of the concentration on the equilibration constants could be detected, most of the equilibration runs were made at a high concentration, generally 0.5 *M*. Under these conditions, the manipulation of these air- and water-sensitive compounds does not require any special technique.

Nevertheless, all the experiments (equilibration and kinetic[4] runs) are always planned[4] to yield ratios of the concentrations of the organosodium compounds (i.e., R_1Na/R_2Na) and not absolute values in such a way as to minimize the effect of a loss of the active sodium.

Determination of the Concentration of the Ions. The equilibrium constant K_{12} is defined as:

$$K_{12} = [R_1Na][R_2H]/[R_2Na][R_1H]$$

Derivatization of the reaction mixture with dimethyl sulfate, trimethyl phosphate, ethyl iodide, and trimethylchlorosilane gave, within the experimental error, the same values of the concentrations.

Samples of the reaction mixture are quenched with an excess of $(CH_3)_2SO_4$ in benzene, the concentration of the four hydrocarbons (R_1H, R_2CH_3, R_1CH_3, R_2H) determined by VPC and the equilibrium constant calculated by the formula:

$$K_{12} = [R_1CH_3][R_2H]/[R_2CH_3][R_1H]$$

Table I. *m*-Xylene/*p*-Xylene Transmetalation Reaction. Influence of the Operating Conditions

Run	Decalin,[a] mol	*m*-Xylene, mol	*p*-Xylene, mol	Polyamine (mol)	Other conditions	K_{mp}[b]
1	0.057	0.024	0.024	TMCHD (0.01)		11.3
2	0.057	0.024	0.024	TMCHD (0.01)	Centrifugation	11.1
3	0.057	0.024	0.024	TMCHD (0.01)	0.048 mol of toluene added	11.0
4	0.057	0.032	0.016	TMCHD (0.01)		11.4
5	0.057	0.008	0.040	TMCHD (0.01)		11.0
6	0.057	0.072	0.072	TMCHD (0.01)		10.7
7	0.057	0.012	0.012	TMCHD (0.01)		11.1
8	0.285	0.120	0.120	TMCHD (0.01)		10.9
9	0.057	0.024	0.024	TMED (0.01)		10.6
10	0.057	0.024	0.024	PMDT (0.01)		11.3
11	0.057	0.024	0.024	HMTT (0.01)		12.1
12	0.057	0.024	0.024	TMCHD (0.01)	0.03 mol of dimethylcyclohexylamine added	7.8[c]

[a] 0.01 mol of C_6H_5Na used in all runs. [b] Constant determined at 25°C; the quench is made with dimethyl sulfate. [c] This value is probably inaccurate, the methylated compounds representing only 60% of the initial organosodium compound. The methylation is always poor when this monoamine is present.

For some of the hydrocarbons investigated, the pure methylated derivatives are not available; it has been shown[8] that the relative response per carbon atom of the flame ionization detector is not very sensitive to the number of carbon atoms in the chain. When necessary, the constant was calculated with the following approximate expression:

$$K_{12} = \frac{(\text{area of peak } R_1CH_3)(\text{area of peak } R_2H)}{(\text{area of peak } R_2CH_3)(\text{area of peak } R_1H)}$$

this approximation being accurate at better than 4%.

Illustrative Example: *m*-Xylene/*p*-Xylene Transmetalation Reaction. A 10-ml portion of a phenylsodium suspension (0.01 mol of C_6H_5Na, 0.01 mol of NaCl, 0.002 g-atom of unreacted sodium, 0.054 mol of decalin) is introduced into the reactor; 0.024 mol of *m*-xylene, 0.024 mol of *p*-xylene, and 0.01 mol of tetramethyl-1,2-diaminocyclohexane (TMCHD) are also introduced into the reactor maintained in a constant-temperature bath at 25 °C, while being swept with nitrogen and agitated by magnetic stirring (see Table I, run 1).

Since the original organosodium compound is insoluble and has not been previously complexed with the diamine, sufficient time (1 hr) is allowed for the attack, i.e., for the diffusion of the amine into the solid. The transmetalation reaction is itself very fast at 25 °C (less than 1 min).

A 2-ml sample is then withdrawn with a syringe and injected into a solution of dimethyl sulfate (0.004 mol) in 2 ml of benzene. The reaction is highly exothermic and sodium sulfate precipitates. After treatment with an excess of dilute hydrochloric acid, the hydrocarbon layer is analyzed by VPC, on a 17 ft × ⅛ in. column, with a stationary phase of bentone 34 and dinonyl phthalate. The equilibrium constant is calculated with the formula:

$$K_{mp} = \frac{(\text{area of } m\text{-ethyltoluene})(\text{area of } p\text{-xylene})}{(\text{area of } p\text{-ethyltoluene})(\text{area of } m\text{-xylene})}$$

It has been verified that the benzene has lost all of its sodium since no toluene is detected in the chromatogram. In this run and in all the other runs, more than 95% of the initial organic sodium is transformed into methylated compounds; the only exception is run 12, where for an unknown reason the presence of a large amount of a monoamine lowers the yield of the methylated compounds.

The contents of the reaction flask was then transferred to a centrifugation tube purged with nitrogen. After centrifugation at 4000 rpm, the clear, highly colored solution was analyzed as in run 1. The equilibrium constant obtained is indicated in Table I, run 2. This shows that centrifugation of the NaCl and excess sodium is not necessary.

In run 2, the compositions of the methylation compounds correspond also to a yield higher than 95%, and this indicates that in runs 1 and 2 the xylylsodium compounds were completely solubilized.

Results and Discussion

Features of the Transmetalation Reaction. The hydrogen-metal exchange reaction (eq 1), also called transmetalation reaction, is not well described, and this is especially the case with hydrocarbons of low acidity and organosodium compounds. The essential features of this reaction will be described first; other features will be further illustrated in a later publication.

Phenylsodium releases all its sodium to the alkylaromatics in excess since the acidity of benzene is sufficiently low. In any case, the presence of a third hydrocarbon, R_3H, does not modify the equilibrium constant K_{12} even when R_3H takes a large part of the sodium. This is illustrated in run 3 in which toluene has been added and participates in the transmetalation equilibria.

It has also been shown that K_{12} is not sensitive either to the relative concentration R_1H/R_2H (runs 4 and 5), to the total alkylaromatic concentration $(R_1H + R_2H)$/alkane (runs 6 and 7), or to the total organosodium concentration $(R_1Na + R_2Na)$/hydrocarbon (run 8). The chelation with the polyamine is consequently the important characteristic of these complexes, and it renders these systems free from the complications usually observed[9] in organoalkali metal chemistry.

The reaction between R_1H and R_2Na is fast at 25 °C, and equilibrium is always obtained in less than 1 min. This is only the case when R_2Na has first been prepared from the phenylsodium–polyamine complex. The chelation of phenylsodium by the polyamine is not very fast since the amine must diffuse into the particles of the suspension; it may take up to 20 min at 50 °C to transform the nonchelated phenylsodium to chelated and soluble R_2Na.

It is known[10,11] that polymetalation compounds are often made in the metalation reaction. We have noted that the constants K_{12}, relative to the monometalated compounds, are not affected by the presence of the dimetalates. Even so, dimetalation can be prevented by operating with a large excess of $(R_1H + R_2H)$.

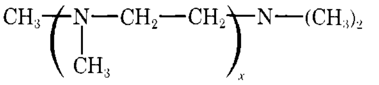
Influence of the Chelating Base. Another diamine (TMED), a triamine (PMDT), and a tetramine (HMTT) have been tested, and the data for the *m*-xylene/*p*-xylene transmetalation are indicated in Table I (runs 9–11). In a previous publication[4] we have shown that the rate constant of the reaction:

$$R_1H + R_2^{-}Li^{+}(\text{polyamine}) \xrightarrow{k_1}$$

varies according to the following expression:

$$k_1 = k_0 100^x \qquad (x = 0, 1, \text{or } 2)$$

where x represents the parameter of the formula:



$$CH_3\text{—}\left(\underset{CH_3}{\underset{|}{N}}\text{—}CH_2\text{—}CH_2\right)_x\text{—}N\text{—}(CH_3)_2$$

Table II. Summary of Equilibrium Constants

R_1H	R_2H	K_{12}
m-Xylene	*p*-Xylene	11.0
p-tert-Butyltoluene	*p*-Xylene	1.2
Mesitylene	*p*-Xylene	11.5
p-Xylene	Cumene	180
p-Xylene	Ethylbenzene	7.7
1,2,4-Trimethylbenzene (2 position)	*p*-Xylene	4.5
m-Cymene	*p*-Xylene	3.7
p-Cymene	*p*-Xylene	0.9
o-Cymene	*p*-Xylene	1.2
Toluene	*p*-Xylene	8.9
o-Xylene	*p*-Xylene	14.3
1-Ethylnaphthalene	Toluene	6.0
2-Ethylnaphthalene	Toluene	2.5
1-Methylnaphthalene	Toluene	105
2-Methylnaphthalene	Toluene	48
3-Methylbiphenyl	Toluene	3.0
Diphenylmethane	1-Methylnaphthalene	132

Table III. Relative Equilibrium Acidities

Hydrocarbon	*K* (per H)	Δp*K*
Cumene	1.87×10^{-3}	+2.73
Ethylbenzene	2.19×10^{-2}	+1.66
p-Xylene	5.16×10^{-2}	+1.25
p-Cymene	1.01×10^{-1}	+1.00
p-tert-Butyltoluene	1.35×10^{-1}	+0.87
o-Cymene	1.37×10^{-1}	+0.87
m-Cymene	4.10×10^{-1}	+0.39
Mesitylene	4.23×10^{-1}	+0.37
1,2,4-Trimethylbenzene (2 position)	5.06×10^{-1}	+0.30
m-Xylene	6.18×10^{-1}	+0.21
o-Xylene	8.03×10^{-1}	+0.10
Toluene	1	0
3-Methylbiphenyl	3.00	−0.48
2-Ethylnaphthalene	3.80	−0.58
1-Ethylnaphthalene	9.00	−0.95
2-Methylnaphthalene	4.80×10^{1}	−1.68
1-Methylnaphthalene	1.05×10^{2}	−2.02
Diphenylmethane	2.08×10^{4}	−4.32

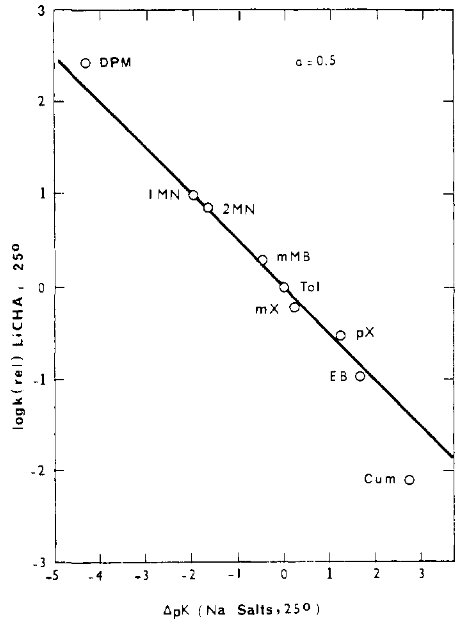


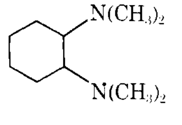
Figure 1. Bronsted correlation of the relative rates of hydrogen isotope exchange with lithium cyclohexylamide and the equilibrium constants of the sodium salts of the alkylarenes.

The number of coordination sites does not appear to have a large effect (other than steric for ethylbenzene or cumene) on the *equilibrium constants*, and the choice of the amine was essentially made on the basis of the following considerations.

(a) The stability of the polyethylene polyamines in the presence of the organoalkali ion pairs at high or medium temperature (50 °C) is not very high as has already been observed[10] for the diamine (TMED); the stability of the triamine (PMDT) and of the tetramine (HMTT) is even lower.

(b) The increase in size of the amine is in many cases unfavorable for the dissolution of the organosodium compounds.

The best overall choice among the four amines investigated was the tetramethyl-1,2-diaminocyclohexane (TMCHD) of formula:



The stability of this diamine is excellent even at 100 °C, and this is probably due to the cyclohexanic nature of the ring which cannot be metalated. The basic strength of this amine (cation solvating power) appears to be superior to the basic strength of the TMED if we can deduce it from the increased solubility of the chelates. In the following we shall refer only to the equilibrium data obtained with this diamine (Table II). The diamine used was a mixture of trans and cis (⅔ trans, ⅓ cis); no attempt has been made to obtain the pure isomers.

Runs were made to determine the acidity constants of 4-methylbiphenyl and triphenylmethane; the results were erratic, and this may be due to the very low solubility of the complexes. The constants obtained with diphenylmethane and cumene are probably less accurate since the cross-checks with various indicators were not possible.

From Table II and with toluene as a reference, the acidity constants of the hydrocarbons listed in Table III have been calculated; Δp*K* refers to $-\log (K/K_{\mathrm{Tol}})$.

As can be seen from Table III, the range of p*K* covered is equal to 7, and, of course, it would be very interesting to obtain a Bronsted correlation for the reaction. Unfortunately, we have not measured the hydrogen-sodium exchange rates; the rate is too fast to be conveniently measured at 25 °C, and at lower temperatures we have encountered difficulties with the solubilities of the organosodium compounds.

The rate data of Streitwieser et al.[2,12] have been used instead, and the Bronsted plot is represented in Figure 1. These data have been obtained by tritium exchange with LiCHA or by deuterium exchange with LiCHA.[13]

The equilibrium constants of the two extreme points (diphenylmethane and cumene) being less accurate, a straight line has been drawn through the other points with a slope α = 0.5, and it seems to give a fair representation of these intermediate points. The kinetic data of Shatenshtein[3] are included in Table IV. For those hydrocarbons less acidic than toluene, the agreement with our data is very good.

The slight deviations apparent in Table IV are relatively small, and the carbanion character of these ion pairs is by now well established. We have, in fact, observed that the hydrogen-metal exchange reaction between *m*-xylene and *p*-xylene (R_1H = *m*-xylene, R_2H = *p*-xylene) is to some extent influenced by the cation and the amine as is shown in Table V.

Variations of the equilibrium constants of ethylbenzene and cumene have also been noted; see Table VI.

Table IV. Relative Hydrogen Exchange Rates

Compound	Streitwieser et al., (LiCHA in CHA)	Shatenshtein et al., (NH_2K in NH_3)	Calculated from Figure 1 with $\alpha = 0.5$
Diphenylmethane (DPM)	269		145
1-Methylnaphthalene (1MN)	10.3		10.2
2-Methylnaphthalene (2MN)	7.4		6.9
3-Methylbiphenyl (mMB)	2.0		1.75
Toluene (Tol)	1	1	1
o-Xylene (*o*X)	0.60	0.97	0.90
m-Xylene (*m*X)	0.60	0.70	0.78
p-Xylene (*p*X)	0.30	0.23	0.28
Ethylbenzene (EB)	0.11	0.14	0.15
Cumene (Cum)	0.0079	0.03	0.04

Table V. Influence of the Cation and the Amine on the Equilibrium Constant for *m*-Xylene–*p*-Xylene

Cation	Amine	K_{12}
Li	TMED	4[4]
Li	PMDT	6[4]
Na	TMED	11
Na	TMCHD	11
Na	HMTT	12
K	HMTT	14[14]

Table VI. Influence of the Cation and the Amine on the Acidity of Ethylbenzene and Cumene

R_1H	R_2H	Na–TMCHD	Na–HMTT	K–HMTT[14]
p-Xylene	Ethylbenzene	7.7	1.6	0.4
p-Xylene	Cumene	180		3

A bulky cation-amine combination seems to displace the equilibrium in favor of the more crowded salt. A possible explanation for this phenomenon is the observation[15] that tertiary benzylic metal compounds have a strong tendency to exist as loose or solvent-separated ion pairs; this effect would be due to the steric hindrance of the methyl substituents at the benzyl position. The sodium or potassium compounds of *p*-xylene, even when they are chelated to a tetramine (HMTT), may exist as a tight or contact ion pair.[16] The situation corresponding to the two reactions reported in Table VI would be very similar to the one reported by Streitwieser et al.[17-19] for solvent and ion-pair effects on the equilibrium constants of the lithium or cesium salts, or more exactly on the steric effect of the alkyl group of 9-alkylfluorenes.[20,21] The kinetic data of Streitwieser et al. reported in Table IV refer to the attack of hydrocarbon by a less bulky ion pair (LiCHA), and the results are probably less influenced by the steric effect; this could explain the deviation of cumene from the Bronsted plot in Figure 1.

Another feature of the data in Table II deserves some attention: *p*-isopropyltoluene (*p*-cymene) and *p*-*tert*-butyltoluene are both more acidic than *p*-methyltoluene (*p*-xylene), and this trend (increase of the acidity with the size of the *p*-alkyl substituent) could well be related to the similar trend observed in the gas-phase acidities of the substituted phenols.[22]

References and Notes

(1) Address correspondence to this author at IPSOI, Rue Henri Poincaré, 13013 Marseille, France.

(2) A. Streitwieser, Jr., M. R. Granger, F. Mares, and R. A. Wolf, *J. Am. Chem. Soc.*, **95**, 4257 (1973).

(3) A. I. Shatenshtein, *Adv. Phys. Org. Chem.*, **1**, 162 (1963).

(4) G. Gau, *Bull. Soc. Chim. Fr.*, 1942 (1972).

(5) M. W. T. Pratt and R. Helsby, *Nature (London)*, **184**, 1694 (1959).

(6) J. F. Nobis and L. F. Moormeier, *Ind. Eng. Chem.*, **46**, 539 (1954).

(7) Monsanto Chemical Company, British Patent 716 649.

(8) W. A. Dietz, *J. Gas Chromatogr.*, **5**, 68 (1957).

(9) A. A. Morton, "Solid Organoalkali Metal Reagents", Gordon and Bresch, New York, N.Y., 1964.

(10) A. W. Langer, "Polyamine-Chelated Alkali Metal Compounds", *Adv. Chem. Ser.*, **No. 130** (1974).

(11) G. B. Trimitsis, A. Tuncay, and R. D. Beyer, *J. Am. Chem. Soc.*, **94**, 2152 (1972).

(12) A. Streitwieser, Jr., and H. F. Koch, *J. Am. Chem. Soc.*, **86**, 404 (1964).

(13) A. Streitwieser, Jr., and W. C. Langworthy, *J. Am. Chem. Soc.*, **85**, 1757 (1963).

(14) G. Gau, unpublished data.

(15) G. Fraenkel, J. G. Russell, and Y. H. Chen, *J. Am. Chem. Soc.*, **95**, 3208 (1973).

(16) F. J. Kronzer and V. R. Sandel, *J. Am. Chem. Soc.*, **94**, 5750 (1972).

(17) A. Streitwieser, Jr., E. Ciuffarin, and J. H. Hammons, *J. Am. Chem. Soc.*, **89**, 63 (1967).

(18) A. Streitwieser, Jr., C. J. Chang, and W. B. Hollyhead, *J. Am. Chem. Soc.*, **94**, 5292 (1972).

(19) A. Streitwieser, Jr., C. J. Chang, W. B. Hollyhead, and J. R. Murdoch, *J. Am. Chem. Soc.*, **94**, 5288 (1972).

(20) L. L. Chan and J. Smid, *J. Am. Chem. Soc.*, **90**, 4654 (1968).

(21) A. Streitwieser, Jr., C. J. Chang, and D. M. E. Reuben, *J. Am. Chem. Soc.*, **94**, 5730 (1972).

(22) R. T. McIver, Jr., and J. H. Silvers, *J. Am. Chem. Soc.*, **95**, 8462 (1973).