Tetrahedron Letters No. 42, pp. 3931 - 3934, 1971. Pergamon Press. Printed in Great Britain.

ACIDITY OF HYDROCARBONS. XL. KINETIC ACIDITIES OF α-ALKYLTOLUENES.

A. Streitwieser, Jr., P. C. Mowery and W. R. Young*

Department of Chemistry, University of California
Berkeley, California 94720

(Received in USA 3 August 1971; received in UK for publication 30 September 1971)

For several years, we have been investigating various theories of organic reactivity by studying the kinetics of hydrogen isotope exchange of weak carbon acids with lithium- (LiCHA) and cesium cyclohexylamide (CsCHA) in cyclohexylamine (CHA) (1). We report here some investigations which indicate the relative importance of steric and polar inductive effects on benzylic acidities in LiCHA-CHA.

The kinetic acidities of α-substituted toluenes were measured in LiCHA-CHA at 50°, and were correlated with σ^* constants for the alkyl substituents; the results are summarized in Table I and Figure 1. The rates of tritium incorporation were measured for 1,2-diphenylethane and toluene in one run, and the kinetic data were analyzed by the LSKIN1 program (2). The protodetritiation rates of 1-phenylpropane-1-d(t) and 2,2-dimethyl-1-phenylpropane-1-d(t) were measured relative to ethylbenzene, and the kinetic data were analyzed with the Perrin program (3); the relative rate for sec-butylbenzene has been published (4). The value for cumene was calculated from earlier protodedeuteration data (5) assuming that the primary isotope effect is the same as that for toluene-α-d(t) (6). Isotope effects were measured in run Y4 and are included in Table I. They show that this assumption is reasonable and will not affect the conclusions. The compounds were labeled by preparing the Grignard reagents from the corresponding benzyl halides and quenching with tritiated D_2O. The kinetic runs were conducted by standard procedures which have been detailed elsewhere (6); the deuterium points were analyzed by low voltage mass spectrometry.

The plot of the kinetic data versus σ^* in figure 1 shows a good correlation.

---

*National Science Foundation Predoctoral Fellow, 1964-6.

TABLE I. Benzylic Proton Kinetic Acidities in LiCHA at 50°

Run	Compound	$10^5 (k_1)_T$ (sec)	k_{rel}	k_D/k_T	σ* (Ref. 15)
M-1	1,2-diphenylethane	4.8 ± 0.1	0.50		0.215
	toluene	9.5 ± 0.6	1.0	2.6[a]	0.49
Y-4	ethylbenzene	0.42 ± 0.1	0.12[b]	2.39 ± .12	0.0
	n-propylbenzene	0.203 ± .005	.059	2.45 ± .09	-.10
	i-butylbenzene	0.045 ± .007	.010	2.87 ± .47	-.19
	neopentylbenzene	0.03	.006		-.30
	sec-butylbenzene		0.0031[c]		-.59
	cumene		0.008[d]		

(a) An average of many results with toluene.

(b) Ref. 16. (c) Ref. 4. (d) Ref. 5.

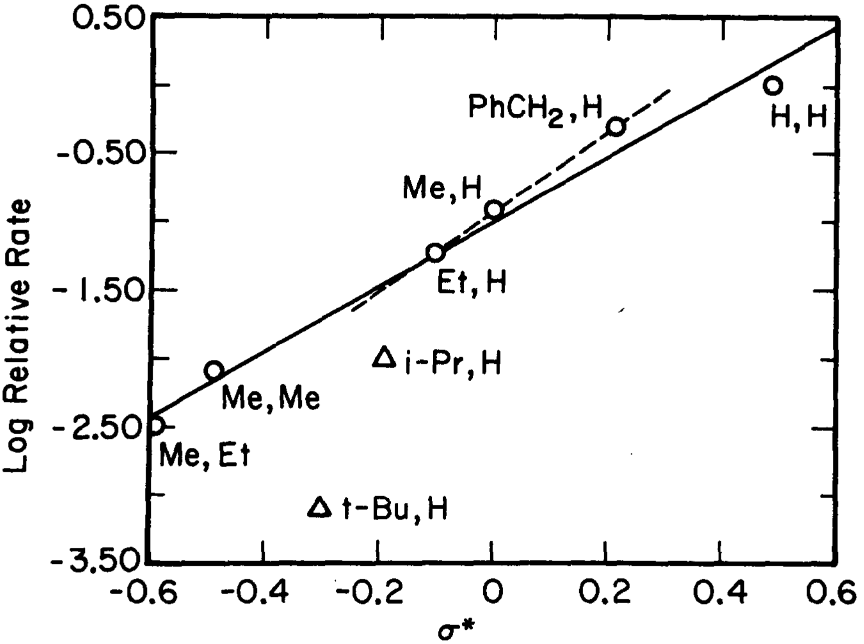

Fig. 1. Tritium exchange of α-alkyl toluenes with LiCHA in CHA at 50°; solid line through circles has corr. coeff. 0.991, slope 2.37, intercept -0.988, std. dev. 0.14. Symbols stand for R,R' in PhCHRR'. Neopentyl- and isobutylbenzenes (triangles) were omitted from the latest squares correlation.

The increasing inhibition of the rates of proton exchange with successive alkyl branching may be due to steric as opposed to inductive effects. However, the rate enhancement of the benzyl group clearly manifests their inductive electronic nature. Isobutyl- and neopentylbenzene fall substantially from the correlation of the other points and clearly exhibit definite steric inhibition to kinetic proton exchange; they were omitted from the correlation. Furthermore, our neopentylbenzene reaction showed little exchange and the relative rate reported in Table I is an upper limit. Since proton exchange in CHA appears to be relatively insensitive to steric hindrance towards the attacking base (4), the observed effect is probably manifest as a steric hindrance to coplanarity in the intermediate benzylic anion. A similar effect has been noted in the corresponding carbonium ions in solvolysis rates of α-alkylbenzyl halides (7).

The destabilizing effect of alkyl groups on carbanions as a function of σ^* demonstrated in the present kinetic acidities is consistent with a comparable effect shown for equilibrium acidities of 9-alkyl and -benzylfluorenes (8). The principal difference is the position of the unsubstituted hydrocarbon. Toluene has higher kinetic acidity than the α-alkyltoluenes whereas fluorene is less acidic than 9-methylfluorene (8,9). However, for proton exchange with methanolic sodium methoxide, 9-methylfluorene is less reactive than fluorene (10). This contrasting pattern of results is explicable in consistent fashion: the conversion from tetrahedral to trigonal carbon is generally facilitated by methyl substituents, but this stabilizing effect on trigonal carbanions is opposed by an electron-donating inductive destabilizing effect. In conjugated carbanions where only a partial negative charge is associated with the substituted carbon, the stabilizing effect dominates and the alkyl substituents enhance acidity. In proton transfer transition states the central carbon is still pyramidal and hybridization stabilization is reduced. Similarly, less charge is delocalized than in the product carbanion; more charge is concentrated at the central carbon and the inductive effect of alkyl substitutents is now dominant. Note that the required postulate of an electron-donating inductive effect for alkyl substituents in solvent differs from the effect observed by Brauman and Blair (11) in the dilute gas phase. In the latter case a dominating role is clearly played by the polarizability of alkyl substituents in the absence of the nearby solvent molecules that reduce this role in solution.

Closer scrutiny of the correlation suggests that the substituent effects may not be best represented by a single line. Instead, it may be dissected into one for trisubstituted methanes (represented by sec-butylbenzene and cumene), and one for disubstituted methanes (n-propylbenzene, ethylbenzene, and 1,2-diphenylethane), with toluene (a monosubstituted methane) being excluded. There is considerable recent evidence that structure-reactivity relationships involving carbanions are more complex than has been previously supposed (12). For example, the Brønsted relationship involving carbon acids comprised of fluorene derivatives and polyphenylmethanes, previously interpreted as a smooth curve (13), has recently been shown to be composed of two separate lines for these two classes (10, 14). The deviations in the present σ^* plot are too small to demonstrate conclusively the presence of such separate sets. Although more data are clearly desirable to fully evaluate this possibility, the present results do demonstrate inductive effects interpretable in a straightforward manner.

Acknowledgement. This research was supported in part by Grant no. GM-12855 of the National Institutes of Health, U.S. Public Health Service.

References

(1) A. Streitwieser, Jr., and G. R. Ziegler, Tetrahedron Lett. No. 5, 415 (1971); A. Streitwieser, Jr., and D. Holtz, J. Org. Chem., 35, 4288 (1970); A. Streitwieser, Jr. and G. R. Ziegler, J. Amer. Chem. Soc., 91, 5081 (1969) and earlier papers.

(2) D. F. Detar, Computer Programs for Chemists, Vol. 1 (New York: W. A. Benjamin and Co., 1968).

(3) A. Streitwieser, Jr., R. G. Lawler and C. Perrin, J. Amer. Chem. Soc., 87, 5383 (1965).

(4) A. Streitwieser, Jr., R. A. Caldwell, R. G. Lawler and G. R. Ziegler, J. Amer. Chem. Soc., 87, 5399 (1965).

(5) A. Streitwieser, Jr., and D. E. Van Sickle, J. Amer. Chem. Soc., 84, 249 (1962).

(6) A. Streitwieser, Jr. and H. F. Koch, J. Amer. Chem. Soc., 86, 404 (1964).

(7) G. Baddeley, J. Chadwick and H. T. Taylor, J. Chem. Soc., 2405 (1954).

(8) C. J. Chang, D.M.E. Reuben and A. Streitwieser, to be submitted.

(9) K. Bowden and A. F. Cockerill, J. Chem. Soc. (B), 173 (1970).

(10) A. Streitwieser, Jr., W. B. Hollyhead, A. H. Pudjaatmaka, P. H. Owens, T. L. Kruger, P. A. Rubenstein, R. A. MacQuarrie, M. L. Brokaw, W. K. C. Chu, and H. M. Niemeyer, J. Amer. Chem. Soc., in press.

(11) J. I. Brauman and L. K. Blair, J. Amer. Chem. Soc., 92, 5986 (1970).

(12) P. C. Mowery and A. Streitwieser, Jr., "Ion-pair Proton Transfers," in Ions and Ion Pairs in Organic Chemistry, M. Swarc, ed. (New York: Wiley-Interscience, Inc., in press).

(13) A. Steitwieser, Jr, W. B. Hollyhead, T. Kruger and A. H. Pudjaatmaka, Abstr. Pet. Div., ACS, 155th Nat. Meeting, 1968; D. J. Cram and W. D. Kollmeyer, J. Amer. Chem. Soc., 90, 1791 (1968).

(14) A. Streitwieser, Jr., W. B. Hollyhead, G. Sonnichsen, A. H. Pudjaatmaka, C. J. Chang, and T. L. Kruger, J. Amer. Chem. Soc., in press.

(15) J. E. Leffler and E. Grunwald, Rates and Equilibria of Organic Reactions (New York: John Wiley and Sons, Inc., 1963), p. 222.

(16) A. Streitwieser, Jr., W. C. Langworthy, and D. E. Van Sickle, J. Amer. Chem. Soc., 84, 251 (1962).