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The Acidities of Some Weak Acids[1]

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A simple system for measuring the rate of proton exchange of a weak acid with its environment has been developed. The compounds studied include aromatic hydrocarbons, substituted acetylenes and ketones. A correlation between rate of proton exchange and pK_a is discussed.

It is well-known that many hydrocarbons—particularly acetylenic hydrocarbons and aromatic hydrocarbons possessing a benzylic hydrogen—are weak acids. While several investigations have been made which enable one to place these hydrocarbons in a relative acidity scale, no systematic investigations have been made which have led either to good values of pK_a's for an extended series of these compounds or to data comparing relative acidities of groups of closely related compounds.

In 1930, Wooster and Mitchell[2] investigated the acidities of some aromatic hydrocarbons by observing the equilibrium

$$HA + KNH_2 \underset{}{\overset{NH_3}{\rightleftarrows}} NH_3 + KA \qquad (1)$$

Since most of the salts of these weak acids possess distinct colors it proved possible to relate the acidities of the compounds studied to ammonia. The compounds studied were, for the most part, benzylic hydrocarbons.

Conant and Wheland[3] extended this investigation by studying competitive equilibria of the nature

$$HA + MA^1 \overset{Et_2O}{\rightleftarrows} MA + HA^1 \qquad (2)$$

The position of equilibrium was determined by comparison of the colors of the individual salts and the color exhibited by a competition-type equilibrium or by carbonation of the equilibrium mixture and isolation of products. The latter method is open to question since equilibrium shifts may be more rapid than carbonation, while the former comparisons are, by their nature, incapable of yielding data better than 0.6 to 2.0 pK_a units. The compounds studied included aromatic hydrocarbons possessing benzylic hydrogens, an acetylenic compound and a ketone.

McEwen[4] extended the investigation so as to include some alcohols and amines by using a variation of the colorimetric methods described above and a polarimetric method. The solvent used was benzene.

The simplest expression of acidity that a strong acid has is its acidity constant. One of the most expressive properties that a weak acid has is the rate at which it will exchange its acidic hydrogen for one in solution.

Work in this area has been reviewed by Pearson and Dillon,[5] and is being carried out by Streitwieser,[6] Kreevoy,[7] Long[8] and Shatenshtein.[9]

Pearson and Dillon have tabulated the available exchange rates for acids in the pK_a range 5–20 (β-keto esters, β-diketones, nitro compounds, etc.). A linear correlation was noted for pK_a *vs.* log (exchange rate) for some of these.

Most recently Streitwieser has reported the kinetics of proton exchange between several deuterated hydrocarbons and lithium cyclohexylamide in cyclohexylamine.

Kreevoy has utilized nuclear magnetic resonance as a tool to investigate proton environments in solutions of phenylacetylene in pyridine–water mixtures. Long has used infrared absorption spectroscopy to determine relative rates of H–D exchange between phenylacetylene or acetylene and water in *heterogeneous* media, and tritium labeling to investigate the same phenomenon in homogeneous solution, and Shatenshtein has worked with benzylic hydrocarbons in ND_3. These techniques have obvious disadvantages for the occasional user who wishes to compare a new weak acid with a series of known compounds.

We have used a simple method, readily applied, to follow the rates of H–D interchange in *homogeneous* media according to the equation

$$RH \xrightarrow[Et_3N,\ DMF]{XS\ D_2O} RD \qquad (3)$$

using the infrared absorption of O–H as a tool.

It will be the purpose of this paper (a) to describe the method in detail, (b) to discuss the mechanism of exchange, and (c) to present data covering a series of substituted acetylenes and aromatic hydrocarbons.

Experimental

Reagents.—Dimethylformamide, Matheson, Coleman and Bell, reagent grade, was dried by passing through Molecular Sieve 4A, and distilled. The middle cut was kept in a desiccator over calcium chloride. The triethylamine used was treated in a similar manner.

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(1) A companion study in the ketone series appears in the following paper by H. Schechter, H. J. Collis, R. E. Dessy, Y. Okuzumi and A. Chen, *J. Am. Chem. Soc.*, **84**, 2905 (1962).

(2) C. B. Wooster and N. W. Mitchell, *ibid.*, **52**, 688 (1930).

(3) J. B. Conant and G. W. Wheland, *ibid.*, **54**, 1212 (1932).

(4) W. K. McEwen, *ibid.*, **58**, 1125 (1936).

(5) R. G. Pearson and R. C. Dillon, *ibid.*, **75**, 2439 (1953).

(6) (a) A. Streitwieser, Jr., D. E. Van Sickle and W. C. Longworthy, *ibid.*, **84**, 244 (1962); (b) A. Streitwieser, Jr., and D. E. Van Sickle, *ibid.*, **84**, 249 (1962); (c) A. Streitwieser, Jr., W. C. Longworthy and D. E. Van Sickle, *ibid.*, **84**, 251 (1962); (d) A. Streitwieser, Jr., and D. E. Van Sickle, *ibid.*, **84**, 254 (1962); (e) A. Streitwieser, Jr., D. E. Van Sickle and L. Reif, *ibid.*, **84**, 258 (1962); (f) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1962.

(7) H. Charman, G. Tiers, M. Kreevoy and G. Filipovich, *J. Am. Chem. Soc.*, **81**, 3149 (1959); Prof. M. Kreevoy, personal communication.

(8) P. Ballinger and F. A. Long, *J. Am. Chem. Soc.*, **81**, 3148 (1959). While this work was being prepared for publication, another article by Long appeared (*ibid.*, **83**, 2809 (1961)) on the mechanism of acetylenic hydrogen exchange. Contrary to the earlier report of specific base catalysis, his more recent work substantiates general base catalysis. His findings and the data presented in this paper are in complete agreement.

(9) A. I. Shatenshtein, *Doklady Akad. Nauk S.S.S.R.*, **60**, 1029 (1959), *et seq.*

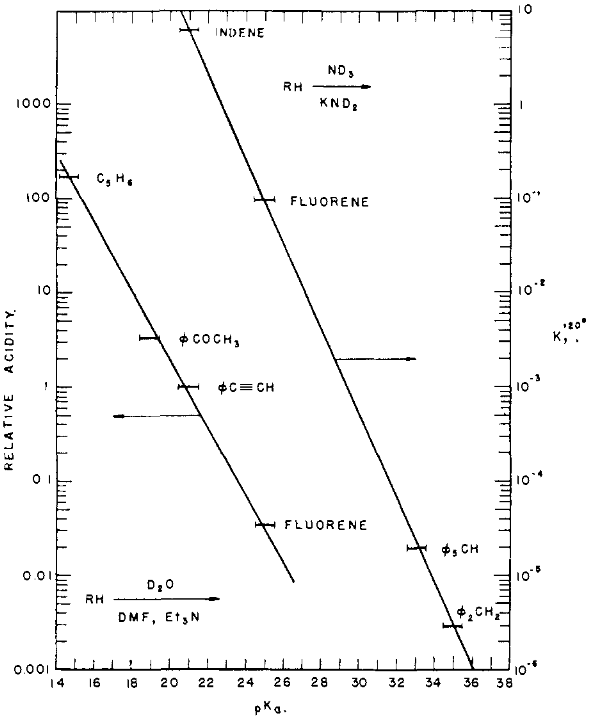

Fig. 1.

Triethylamine deuteriochloride was prepared by the addition of DCl gas (Merck and Co., Ltd.) to triethylamine. Excess amine was removed under vacuum, leaving pure deuteriochloride, m.p. 253°.

Sodium deuteroxide was prepared by treating freshly cut sodium with absolute methanol. Excess methanol was removed under vacuum, and the resulting sodium methoxide treated with deuterium oxide. The product was dried at 100° under a vacuum.

The inorganic salts used were analytical reagents, oven-dried before use.

The phenyl cycloalkyl ketones were obtained from Prof. Harold Shechter, and were redistilled shortly before use.

Cyclopentadiene was obtained by thermal decomposition of its dimer, b.p. 42°.

Fluorene, Matheson, Coleman and Bell, was recrystallized before use; m.p. 116°.

The acetylenes were purchased commercially or obtained from private laboratories. Gaseous materials were purified by passage through sulfuric acid and Molecular Sieves; liquid materials were distilled shortly before use and stored in sealed ampoules under nitrogen; solid materials were recrystallized.

Kinetic Procedure.—The rates of exchange of deuterium for the active hydrogen of weak acids in the system

$$RH + xD_2O \xrightarrow[Et_3N]{DMF} RD + DOH + (x - 1)\,D_2O$$

were measured spectrophotometrically by following the absorption due to the DOH species which result from the D/H exchange. The stretching frequency for the O–H band occurs near 2.8 μ. As the solvent environment changes, the position of the peak shifts somewhat, but never more than 0.1 μ.

All of the measurements were made on a Beckman IR-2 single beam infrared spectrophotometer, thermostated at 30°. Cells with sapphire windows and 0.1 mm. spacers were employed. Working curves relating optical density (A) and concentration [(O–H)] for the solvent systems were made by adding known amounts of H_2O to them. For the system D_2O–DMF the relationship (O–H) = $1.21A + 0.75$ was obeyed, while the other systems with amine present obeyed the relationship (O–H) = $1.31\,A + 0.50$.

In a typical run, a temperature equilibrated solution of of the weak acid in the DMF–Et_3N solvent system was mixed with a temperature equilibrated solution of the D_2O (Liquid Carbonic Div., General Dynamics, 99.5%) in DMF (predilution of the D_2O is necessary because of its high heat of solution). Samples were withdrawn from the thermostated reaction vessel, and A (% T) measured as indicated above for some 15 to 50% of the reaction coördinate.

Since the reactions are run under approximately pseudo-first-order conditions, an "active H/D" ratio of 10/1, the slopes of plots of log $(a^2/(a^2 - ax))$ vs. t gave k_1 directly; reversibility of the exchange would not become important until about 50% exchange occurred and therefore during the initial stages of the exchange (0–35%) the data can be accommodated by simple first-order expression rather than a reversible one (a = concn. of weak acid HA at t_0, x = concn. of DA at t).

The temperature ranges involved were from 0–80°. In all cases runs were made in duplicate. Reproducibility was ±4%. Extrapolations to 40° in a few cases were made by log k vs. $1/T$ plots. Blank runs indicated that over the time period and temperatures employed (80° for 1 week) no exchange with the solvent DMF occurred.

Lithiopropyne–D_2O Reaction.—To a solution of 0.1 mole (0.7 g.) of lithium in 30 ml. of liquid ammonia was added slowly propyne until the characteristic blue color disappeared. The solvent was removed with a stream of dry nitrogen, and the resulting white powder was subjected to a vacuum of 1 mm. for 5 hours at 50°. The lithiopropyne was stored in a dry-box under argon until needed.

To a solution of 0.01 mole (0.46 g.) of lithiopropyne in 5 ml. of dioxane was added 0.02 mole (0.4 g.) of deuterium oxide, under vacuum. Propyne-*d*-1 gas evolved from the solution, and a sample was analyzed by mass spectrometry (U. S. Industrial Chemical Co., Cincinnati, O.). The composition was found as C_3H_3D, 95.9%; C_3H_4, 4.1%.

To a similar solution of 0.01 mole (0.46 g.) of lithiopropyne was added a mixture of 0.008 mole (0.16 g.) of deuterium oxide and 0.012 mole (0.216 g.) of water. Analysis of the propyne evolved gave: C_3H_3D, 37.5%; C_3H_4, 62.5%.

Results and Discussion

The requirements of a system to be used to study H–D interchange are a suitable solvent and catalyst. The solvent must be one capable of miscibility with D_2O and capable of dissolving organic compounds in relatively high concentrations if infrared spectroscopy is to be used as a tool. Dimethylformamide (DMF) was the only solvent found which possessed these characteristics. The catalyst must give uniform results with widely different activating sources, and must not cause spurious salt effects or give rise to steric effects. Long[8] found that acid catalysis was ineffective in the acetylenic series, so base catalysis was sought. Attempts to use sodium deuteroxide as a catalyst were not fruitful, as Table I indicates. Table I compares the exchange rate for several ketones and phenylacetylene using both sodium deuteroxide and triethylamine as catalysts. Although the k_{NaOD}/k_{Et_3N} ratio is constant for a series of ketones with varying steric requirements, the ratio varies markedly between the ketones and phenylacetylene. A salt effect seems responsible for the deviations which may be attributed to sodium deuteroxide as Table I also shows. Such an interaction might be pictured as

$$\begin{array}{c} R\text{—}C{\equiv}C\text{—}H \\ \downarrow \\ M^+ \end{array}$$

Metal–π-cloud interactions of this type are of course quite familiar with mercury or silver.[10,a,c]

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[10] (a) H. Lemaire and H. J. Lucas, *J. Am. Chem. Soc.*, **77**, 939 (1955); (b) H. Pines and L. A. Schaap, *Advances in Catalysis*, **12**, 121 (1960); (c) *cf.* Ag^+ complexes, F. R. Hepner, K. N. Trueblood and H. J. Lucas, *J. Am. Chem. Soc.*, **74**, 1333 (1952); (d) R. S. Stearns and L. E. Forman, Abstracts, 134th Meeting of the American Chemical Society, Chicago, Ill., September, 1958, p. 12-U.

TABLE I

$$\underset{1\,M}{\mathrm{RH}} \xrightarrow[\text{DMF, } 5\,M\ \mathrm{D_2O}\ \text{(salt)}]{\text{Base}} \mathrm{RD}^{a}$$

Base	Concn., m./l.	k_1^{40}, sec.$^{-1}$ × 10^5 $C_6H_5C{\equiv}CH$	 $C_6H_5COCH_3$	 $C_6H_5COCH_2CH_3$	 $C_6H_5COCH(CH_3)_2$	 Cyclo-$C_4H_7COC_6H_5$	 Cyclo-$C_5H_9COC_6H_5$
Et_3N	1.0	6.6	22	4.9	0.0065	0.084	0.029
NaOD	0.02	3.3	..	6.0	0.010	0.099	0.042
k_{NaOD}/k_{Et_3N}		5.0	..	1.2	1.5	1.2	1.4
Salt							
LiCl	0.02	7.3	..				
NaCl	.02	7.6	1.2				
KCl	.02	1.3	..				
Et_4NI	.02	1.2	..				
No catalyst		0.40	1.1				
$k_{salt}/k_{no\ cat.}$		3–19	1.0				

[a] All rates are corrected for the statistical factor.

but references involving interactions with alkali metals are rare. Pines[10b] has semi-seriously suggested that similar complexing in olefin–alkali metal systems may explain the isomerization of butene-1 to *cis*-butene-2 in a kinetically controlled step, the *cis*-butene-2·Na^+ complex being more stable than the *trans*-butene-2·Na^+ complex.[10c] Stearns[10d] has used a similar argument to explain the all-*cis* polymerization of dienes by lithium.

It is apparent that as the charge/surface area ratio (charge density) decreases the extent of interaction decreases, as would be expected if the ability of the cation to polarize the unsaturated linkage were important, and back bonding were relatively unimportant.

In Long's work[8] these salt effects were not recognized, and since NaCl, KCl and NH_4Cl were used variously to maintain constant ionic strength it is probable that his absolute rate constants are not valid—however, his interpretations are not seriously affected. Because of such salt effects it appeared most logical to employ Et_3N as a catalyst.

Table II shows the effect of increasing the amine concentration on the rate of exchange.

TABLE II

$$\underset{1\,M}{C_6H_5C{\equiv}CH} \xrightarrow[\text{DMF, } 5\,M\ \mathrm{D_2O}]{\mathrm{Et_3N}} C_6H_5C{\equiv}CD$$

Et_3N concn., m./l.	k_1^{40} (sec.$^{-1}$) × 10^5	Et_3N concn., m./l.	k_1^{40} (sec.$^{-1}$) × 10^5
0.05	3.8	0.70	10.7
.10	5.7	.90	7.3
.20	9.5	1.0	6.6
.30	10.8	2.0	6.2
.50	11.2		

West[11a] has shown that DMF is basic enough to affect the ≡C—H frequency in acetylenes by hydrogen bonding while Kreevoy has shown the importance of terminal acetylene–amine hydrogen bonding.[11b] Formation constants for terminal acetylene–pyridine "hydrogen bonded" complexes in carbon tetrachloride were found to be of the order of 0.25. It seemed wise to use a large excess of triethylamine as a catalyst in order to ensure that varying amounts of solvent, catalyst hydrogen bonded interaction did not interfere with the kinetic picture. One molar amine was chosen since the absolute rate of exchange is a function of (Et_3N), passing through a maximum near 0.5 M and leveling off at ~ 1.0 M. A large excess of D_2O seemed advisable also, because of the simplification of kinetics and the minimization of possible isotope effects.

TABLE III

$$\underset{1\,M}{C_6H_5C{\equiv}CH} \xrightarrow[\text{DMF, } 5\,M\ \mathrm{D_2O}]{\mathrm{Et_3N,\ Et_3N{\cdot}DCl}} C_6H_5C{\equiv}CD$$

Concn. Et_3N, m./l.	Concn. $Et_3N{\cdot}DCl$, m./l.	k_1^{40} (sec.$^{-1}$) × 10^5	Concn. Et_3N, m./l.	Concn. $Et_3N{\cdot}DCl$, m./l.	k_1^{40} (sec.$^{-1}$) × 10^5
..	..	0.40	0.20	0.20	1.7
..	0.05	.057	.30	.30	1.9
..	.10	.052	.025	.20	0.21
..	.20	.042	.05	.20	.32
0.05	.05	.47	.10	.20	.56
.10	.10	1.1			

The system finally chosen was 1 M Et_3N, 5 M D_2O, 1 M substrate, in DMF.

Mechanism of Exchange.—In the system chosen two bases are available as catalysts. Table III

$$\mathrm{Et_3N + D_2O \rightleftharpoons Et_3ND^+ + OD^-} \qquad (4)$$

indicates the studies made of the effect of $Et_3N{\cdot}DCl$ on the rate of exchange of $C_6H_5C{\equiv}CH$. In the absence of Et_3N it markedly decreases the rate, small amounts having a marked effect, apparently by reducing the catalytic activity of the DMF–D_2O solvent system. The change in rate from 0 to 0.05 M $Et_3N{\cdot}DCl$ involves a factor of 10. The change involved in passage from 0.05 to 0.20 M $Et_3N{\cdot}DCl$ is about 30%. Reactions run with identical ratios of (Et_3N)/($Et_3N{\cdot}DCl$) show $k_1 \propto (Et_3N)$ suggesting general base catalysis; however, such runs are always subject to salt effects.[12] More definite information is supplied by data from runs in the presence of a large excess of $Et_3N{\cdot}DCl$ to repress ($OD^{\ominus}$). They also indicate a linear relationship between k_1 and Et_3N. The data suggest therefore general base catalysis, similar to the recent findings of Long.[8] Rough calculations, ignoring salt effects, using the data in Tables I and III suggest that $k_{OD^{\ominus}}$ is at least 100 times larger than k_{Et_3N}, and that "Et_3N catalysis" really involves catalysis by $OD^{\ominus}$.

This is confirmed by the fact that E_a values for $OD^{\ominus}$ and "Et_3N" catalysis are identical, (*e.g.*

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(11) (a) R. West and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **83**, 765 (1961); (b) M. M. Kreevoy, H. B. Charman and D. Vinard, *ibid.*, **83**, 1979 (1961).

(12) See R. P. Bell, "Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 78, for a general discussion of the methods employed.

TABLE IVa

$$\begin{matrix}\text{RC}\equiv\text{CH} \\ \text{or} \\ \text{ZC}_6\text{H}_4\text{C}\equiv\text{CH} \\ 1\ M\end{matrix} \xrightarrow[\text{DMF, } 5\ M\ \text{D}_2\text{O}]{1\ M\ \text{Et}_3\text{N}} \begin{matrix}\text{RC}\equiv\text{CD} \\ \text{or} \\ \text{ZC}_6\text{H}_4\text{C}\equiv\text{CD}\end{matrix}$$

R	R.A.	k_1^{0}	k_1^{20}	k_1^{30} (sec.$^{-1}$) × 10^{5a}	k_1^{40}	k^{60}	k_1^{65}	E_a	$\Delta S^{\ddagger}$
C_6H_5–	1.0	..	..	...	6.6	40	...	18.5	−21
H–	0.73	..	..	...	4.8	...	...	..	..
C_4H_9–	.058	0.1	..	...	0.38	1.9	...	17.8	−39
$Cl(CH_2)_4$–[b]	.033	..	..	...	.22	0.89	3.7	16.8	−33
$HC\equiv C(CH_2)_4$–[b]	.076	0.32	..	...	.50	1.9	...	14.6	−37
$HC\equiv C(CH_2)_4C\equiv C(CH_2)_4$[b]	.081	..	..	...	.53	2.4	...	16.2	−32
CH_3O–	2.0	..	..	7.6	13	49	...	11.0	−44
$(C_6H_5)_3Si$–[c]	68	..	..	230	450	...	...	..	..
Z									
H	1.0	..	..	...	6.6	40	...	18.5	−21
o-F[d]	4.7	..	..	...	31	...	...	..	..
m-F[d]	7.7	..	..	...	50	...	...	..	..
p-F[d]	1.5	..	..	...	10	23	...	16.2	−22
o-CF_3[d]	3.5	..	..	...	23	...	...	..	..
m-CF_3[d]	5.2	..	..	...	35	...	...	..	..
p-CF_3[d]	3.3	..	..	...	22	...	...	..	..
m-Cl	28	..	55	100	190	...	...	11.7	−36
p-Cl	4.8	..	..	...	32	...	160	13.8	−32
p-Br	2.1	..	..	...	14	...	78	14.5	−32
p-CH_3O	1.0	..	..	...	6.6	28	...	14.9	−32
p-$HC\equiv C$—[e]	13.8	3.5	..	44	91	...	...	13.9	−29

[a] All rates are corrected for the statistical factor. [b] Kindly supplied by Dr. J. H. Wotiz, Diamond Alkali Co. [c] Kindly supplied by Prof. R. West, University of Wisconsin. [d] Kindly supplied by Prof. R. Filler, Illinois Institute of Tech. and Mr. I. Solomon, Armour Research Lab. [e] Kindly supplied by Dr. A. W. Hay, General Electric Co.

for $C_6H_5COCH(CH_3)_2$ 1 *M*, D_2O 5 *M*, Et_3N 1 *M*, in DMF, $k_{60°} = 2.8 \times 10^{-7}$ sec.$^{-1}$, $k_{80°} = 9.5 \times 10^{-7}$; with NaOD, 0.02 *M*, as catalyst, $k_{60°} = 4.3 \times 10^{-7}$, $k_{80°} = 1.4 \times 10^{-6}$: E_a in both cases is 14.2 kcal./mole) and suggested by the fact that a series of C_6H_5COR compounds show a uniform $k_{OD^{\ominus}}/k_{Et_3N}$ ratio (Table I) indicating no serious steric factor is present.

Acidities of Some Hydrocarbons.—Table IVa indicates the rates of exchange for a series of hydrocarbons investigated. Also indicated in Table IVb are the pK_a values for those compounds also investigated by McEwen.[4] Relative acidity values (R.A.) have been calculated from the pseudo-first-order rate constants, assigning a value of unity to the rate of exchange of phenylacetylene in the standard solvent mixture. All values are also corrected for the statistical factors.[13]

TABLE IVb

$$\text{RH} \xrightarrow[\text{DMF, } 5\ M\ \text{D}_2\text{O}]{1\ M\ \text{Et}_3\text{N}} \text{RD}^{a}$$

RH	k_1^{44} (sec.$^{-1}$) × 10^5	R.A.	pK_a[4]
Cyclopentadiene	1100	170	14–15[b]
Acetophenone	22	3.3	19
Phenylacetylene	6.6	1.0	21
Fluorene	0.22	0.033	25

[a] All rates are corrected for the statistical factor. [b] The value of 14–15 assigned to cyclopentadiene is based on unpublished observations from our laboratory that sodium methoxide in methanol will metalate cyclopentadiene, yielding upon carbonation cyclopentadienecarboxylic acid and dicyclopentadienecarboxylic acid. This indicates that cyclopentadiene is a stronger acid than methanol, pK_a 16. Sodium phenoxide fails to metalate cyclopentadiene indicating that cyclopentadiene is a weaker acid than phenol. Recent M.O. calculations by A. Streitwieser also place cyclopentadiene in this range (*Tetrahedron Letters*, 6, 23 (1960)).

The reaction of $CH_3C\equiv CLi$ in dioxane with a 3/2 mixture of H_2O/D_2O gives rise to a mixture of $CH_3C\equiv CH/CH_3C\equiv CD$ in the ratio of 3/2 (mass spectrometric analysis) suggesting that the discharge of an anion, the conjugate base of a weak acid (pK_a = 21), is diffusion controlled. This is supported by other carbanion discharge data.[14] For a weak acid we may write

$$\text{HA} \overset{K_a}{\rightleftarrows} \text{H}^+ + \text{A}^-;\ K_a = k_f/k_r \qquad (5)$$

The above suggests that for weak acids k_r is large and constant, and that K_a should be proportional to k_f.

Kreevoy[15] has reached a similar conclusion. He has recently shown that in the hydroxide ion-catalyzed exchange between acetylenes and aqueous *t*-butyl alcohol the rate-determining step for exchange may be "pictured as the removal of the terminal acetylenic proton by hydroxide ion ($RC\equiv CH + OH^- \rightleftarrows RC\equiv C:^- + H_2O$). The transition state is thought to resemble the products of the rate-determining step (acetylide ion + water) since the reverse reaction must have a very low activation energy." Calculations suggest that almost all of the free energy of activation involved in discharge of an acetylide ion by water is made up of the entropy change involved in water immobili-

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(13) When necessary, k_1^{40} values were calculated from data at other temperatures by means of log k_1 *vs.* $1/T$ plots.

(14) *Cf.* K. Wiberg, *Chem. Revs.*, **55**, 722 (1955).

(15) H. Charman, D. Vinard and M. Kreevoy, *J. Am. Chem. Soc.*, **83**, 347 (1961).

zation, and that less than a kilocalorie of activation energy is involved. Long[3] has shown that the rate of discharge is practically diffusion controlled.

In this light it is interesting to compare the pK_a values of McEwen[4] with the present rate data, and with the data reported by Shatenshtein[9,16] on the pseudo-first-order rates of deuterium-hydrogen exchange in the system (see Fig. 1)

$$RH \xrightarrow[KND_2]{ND_3} RD \qquad (6)$$

The slopes of both straight lines are nearly equal, with a value of 0.4. (Pearson and Dillon,[5] working with much stronger acids, pK_a 5–20, found a slope of 0.6.) These correlations suggest: (a) the transition state for the ionization and the transition state for hydrogen exchange are identical or are similar and have their energies determined by similar processes—$k_f \propto k_1$; (b) the present system (DMF, D_2O, Et_3N) is very similar to ND_3 as a solvent, at least as far as determination of relative acidities is concerned, and data from one may be transferred to the other.

This knowledge of relative rates and the parameters which connect them with pK_a would make it possible to assign values of the latter to compounds for which the former was known (in the present series log (R.A.) = $-0.4pK_a + 8.2$). Although such pK_a's would be estimates only, because of differing solvation pictures as the substrate functional groups change and because of variations in the position of the transition state along the reaction coördinate as activating groups change, it does provide a guidepost in weak acid studies.

As previously mentioned, Table IV shows the data for a series of substituted acetylenes.

Edgell[17] has measured the stretching frequencies of a number of terminal alkynes ($\equiv$C—H) and calculated the force constants involved. In the series RC$\equiv$CH (R = C_4H_9, C_6H_5, $BrCH_2$) this $k_{\equiv C-H}$ is constant, $5.87 \pm 0.05 \times 10^5$ dynes/cm.

Since this suggests that the ground state of the $\equiv$C—H linkage is not affected by the substituents either by inductive or resonance effects and Kreevoy's data suggest a transition state for hydrogen exchange with acetylide ion character and little discharge activation energy, it is apparent that changes in rate of exchange as a result of substituent changes in a series of terminal acetylenic compounds is associated mainly with changes in acetylide ion stability which are reflected by Hammond's principle[18] to the transition state.

Although Kreevoy has pictured the acetylide ion as involving an electron pair in the sp-orbital of C_1, an orbital orthogonal to the π-system, thus preventing resonance interaction, it should be pointed out that an unhybridized C_1 with the pair in an s-orbital might also be involved with similar consequences. Most assuredly the orbital occupied by the lone pair has its p-character greatly reduced.

In any event, following Kreevoy's lead, resonance interaction with the substituents should be at a minimum in the transition state.[19]

It has been demonstrated that transmission of electrical effects through a triple bond is only a little more efficient than through a single bond,[20] so the inductive effects will be muted somewhat.

For the series RC$\equiv$CH, (R = CH_3OCH_2–, $CH_3OC(CH_3)_2$–, $CH_3O(CH_2)_2$–, $HOCH_2CH_2$–) Kreevoy[15] has observed that a plot of log k (where k is the rate of exchange) *vs.* σ^{*21} is linear, $\rho^* = 2.3 \pm 0.2$. The rate spread was about a factor of 10.

Although this suggests that the conclusions above concerning the importance of inductive effects in this reaction are correct, it is not completely satisfactory since most of the σ^*-values used by Kreevoy were calculated values, not average experimental values.

If we accept these assumptions, however, the present system represents a reaction with known geometry in the ground and transition state, where resonance interactions in both ground and transition states are at a minimum, and where only inductive effects, field effects, London dispersion forces[22] and solvation may affect the transition state. In a sense the —C$\equiv$CH unit may serve as a probe—placing it on a group would allow one to evaluate the contribution of the latter factors. When —C$\equiv$CH is replaced by another group, resonance factors may be reintroduced and evaluated. In this light Table IV is of interest.

A number of important general conclusions may be made from these results: (a) The change in going from an aromatic to an aliphatic acetylene is large—some 2 pK_a units. This is in agreement, however, with the work of Gilman[23] who found in a competitive metallation study that heptyne is ~1.5 pK_a units weaker than phenylacetylene. (b) Phenylacetylene and acetylene are approximately of the same acid strength, a fact which confirms the data of Long.[8] (c) As the degree of non-conjugated unsaturation is increased in an acetylenic compound, the relative acidity increases. This might be ascribed to a type of internal hydrogen bonding similar to the intermolecular bonding found by Eglington,[24] or to a field effect. This seems to be supported by the fact that the ratio $k_1^{HC\equiv C(CH_2)_4C\equiv CH}/k_1^{C_4H_9C\equiv CH}$ changes rapidly as a function of temperature approaching unity at higher temperatures as might be expected for a weak intramolecular interaction. The effect of the ω-chloro group could arise in a similar manner. (d) In the substituted phenylacetylenes the pK_a's range from 17 (*m*-Cl) to 21 (H). This is perhaps

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(16) The rate data reported in this paper were in error by a factor of 10 as indicated in a later erratum, *Zhur. Fiz. Khem.*, **25**, 1206 (1951).

(17) Prof. W. Edgell, private communication.

(18) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(19) Kreevoy[7] has evidence based on $\sigma^*\rho^*$ plots that the phenyl, —C$\equiv$C:⊖ resonance interaction is very small *if it does exist.*

(20) R. E. Dessy and J. Y. Kim, *J. Am. Chem. Soc.*, **83**, 1167 (1961).

(21) *Cf.* R. Taft in "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1946.

(22) *Cf.* J. D. Reinheimer and J. F. Bunnett, *J. Am. Chem. Soc.*, **81**, 6573 (1959).

(23) H. Gilman and R. Bell, *ibid.*, **61**, 109 (1939).

(24) J. C. D. Brand, G. Eglinton and J. F. Morman, *J. Chem. Soc.*, 2526 (1960).

a larger range than one might expect, but it seems more reasonable when one considers the same span in the substituted benzoic and boronic acids, and phenols and thiophenols.[25] It is apparent that as the strength of the acid decreases the effect of substituents on the pK_a's increases.

In the aromatic series, with F and CF_3 as substituents, direct inductive effects render the *m*-substituted phenylacetylenes more acidic than the *p*-compounds, but field effects, operating in an acid-weakening manner, render the *o*-substituted compounds less acidic than might be expected. The fact that they are still more acidic than the unsubstituted compound suggests a balance between field and inductive effects, with the latter slightly more important.[5]

Although qualitatively the Cl and Br substituted compounds seem to fit the pattern well, the *m*- and *p*-substituted compounds (F, CF_3, Cl) do not fit the $\sigma_I\rho_I$ expression of Taft,[21] nor does the entire series give a normal Hammett plot. It is encouraging, but somewhat frustrating in light of the above, that the acidity of the series $HC\equiv CH$, $C_4H_9C\equiv CH$, $C_6H_5C\equiv CH$ gives a correlation with σ^*-values.[21]

The large inductive (−I) effect of the $HC\equiv C$— function is to be noted, as should the weak effect of the CH_3O grouping.

It is hoped that this report may encourage further work in the use of the $\equiv C—H$ unit as a probe.[26a,b,c]

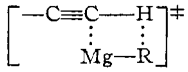
It is significant that this sequence of acidities for various acetylenes does not parallel the "acidities" determined by the rate of reaction with ethylmagnesium bromide[27] (Table V). This suggests

$$\text{"EtMgBr"} + RC\equiv CH \longrightarrow \text{"}RC\equiv CMgBr\text{"} + EtH^{28}$$

TABLE V

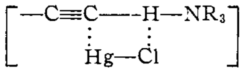
Acetylene	$RC\equiv CH \xrightarrow[DMF,\ Et_3N]{D_2O}$	$RC\equiv CH + \text{"RMgX"} \xrightarrow{Et_2O}$
	Relative rate	
$C_4H_9C\equiv CH$	0.058	1.3
$C_4H_9OC\equiv CH$	..	>6.5
$CH_3OC\equiv CH$	2.0	..
$C_6H_5C\equiv CH$	1	1
p-$BrC_6H_4C\equiv CH$	2.1	1.2
p-$ClC_6H_4C\equiv CH$	4.8	2.2

that the latter is not merely a protolysis reaction, but involves a hindered transition state as suggested earlier. Since complexing has been shown not to be energetically important, taking into account the information available concerning this reaction, it is not unreasonable to suggest a four-center transition state for the process (I) similar to



$$\left[\begin{matrix}—C\equiv C & — & H \\ \vdots & & \vdots \\ Mg & — & R\end{matrix}\right]^{\ddagger}$$

I



$$\left[\begin{matrix}—C\equiv C & — & H—NR_3 \\ \vdots & & \vdots \\ Hg & — & Cl\end{matrix}\right]$$

II

the one proposed for reactions of terminal acetylenes with mercuric salts (II).[29]

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(25) *Cf.* H. C. Brown, D. H. McDaniel and O. Hafliger, in "Determination of Organic Structures by Physical Methods," edited by E. A. Braude and F. C. Nachod, Academic Press, Inc., New York, N. Y., 1955.

(26) (a) The preliminary work on the acidities and rates of esterification of *o*, *m* and *p*-F, and CF_3 substituted phenylpropiolic acids by R. Miller and I. Solomon (unpublished results, personal communication) and similar work by Roberts[26b] and Newman[26c] on the nitro, chloro and methoxy derivative provide some correlations, but much more work is needed; (b) J. D. Roberts and R. A. Carboni, *J. Am. Chem. Soc.*, **77**, 5554 (1955); (c) M. S. Newman and S. H. Merrill, *ibid.*, **77**, 5552 (1955).

(27) J. H. Wotiz, C. A. Hollingsworth and R. E. Dessy, *J. Org. Chem.*, **20**, 1545 (1955).

(28) The structure of the Grignard reagent has been shown to involve an $R_2Mg\cdot MgX_2$ complex. However, it is conceptually easier to write it as "RMgX" rather than as the complex. In the majority of cases whether one uses the true dimeric structure or "RMgX" does not affect the concepts involved.

(29) (a) R. E. Dessy, Wm. Budde and C. Woodruff, *J. Am. Chem. Soc.*, **84**, 1172 (1962); (b) R. E. Dessy, J. H. Wotiz and C. A. Hollingsworth, *ibid.*, **79**, 358 (1957).