the pi complex. Such an explanation works best with the pi complex charge distribution corresponding predominantly to the covalent structure.

Suggested Experiments.—The possibility that the blue violet colors observed by Wittig, Joos and Rathfelder[13] in the acid catalyzed rearrangement of cyclic hydrazobenzenes may be a property of the pi complex, provides a possibly important means of studying the nature of the pi complex and its role in the rearrangement mechanism. They observed these colors during the acid catalyzed rearrangements of N,N′-trimethylene-hydrazobenzene and N,N′-tetramethylene-hydrazobenzene. The color was not reported for the rearrangement of N,N′-pentamethylene-hydrazobenzene. It is reasonable to suppose that in the former two cases the shorter methylene chains greatly slowed the unfolding of the pi complex to products. The observed color may be attributed to the pi complex thus stabilized. The observation of such colors during the acid catalyzed rearrangement in solution has never previously been reported for hydrazocompounds not having a chain joining the nitrogen atoms. These cyclic hydrazocompounds may show during rearrangement additional physical properties which can be correlated with the transient colors and postulated structures for the pi complex.

It is clear that both nuclear magnetic and electron spin resonance spectra should be searched for time dependent features which may be associated with the transient colors and postulated pi complex. The covalent and charge transfer structures should have qualitatively different chemical shifts of the proton resonances, relative to benzene protons. The electron spin resonance spectra may show the transient colors to be associated with the pi complex triplet state, with independent radical fragments, or with an oxidation product of the hydrazocompound.[38] A singlet ground state should give no resonance.

Finally, it is probable that hydrazo derivatives of paracyclophanes[39] can be synthesized. They may react thermally or with acid to provide additional interesting stable pi complexes.

Acknowledgments.—I wish to thank Professor R. B. Carlin and Dr. H. G. Ebner for pointing out relevant knowledge from experiments. Comments on theoretical sections by Professor R. G. Parr have been helpful. Discussions with Dr. A. M. Trozzolo, Dr. R. W. Murray and with Dr. D. E. Wasserman, and Dr. E. A. Chandross also have been of value.

[38] Experiments performed at Bell Telephone Laboratories since the submission of this manuscript support the latter possibility. Studies of the electron spin resonance spectra of the blue solutions which occur during the rearrangement of N,N′-tetramethylene-hydrazobenzene by trifluoroacetic acid in benzene suggest very strongly that the blue color is due to the positive ion produced by oxidation of the hydrazocompound. It is still possible that relatively stable pi complexes may be produced during the rearrangement of the cyclic hydrazocompounds.

[39] D. J. Cram and R. A. Reeves, *J. Am. Chem. Soc.*, **80**, 3094 (1958)

[Contribution from the School of Chemistry, University of Minnesota, Minneapolis 14, Minnesota]

Rates of Proton Abstraction from Monosubstituted Acetylenes

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Rates of hydroxide ion catalyzed proton exchange between six alkynes, R—C≡CH, and aqueous *t*-butyl alcohol have been measured by n.m.r. line broadening techniques. Second-order rate constants have been shown to be independent of the base concentration and assumed to be independent of the alkyne concentration. Four of these define a line of slope (ρ^*) 2.3 when plotted against the Taft σ^* parameters for the groups R. Phenylacetylene gives a rate which misses this line by only 0.3 log unit, in accord with theoretical expectations. The point given by 3,3-diethoxy-1-propyl deviates widely from the correlation line and this is attributed to the relatively slow but complete abstraction of the 3-proton by hydroxide. The rate determining step for exchange is pictured as the removal of the terminal, acetylenic proton by hydroxide ion. The relative ionization constants of alkynes are thought to be governed by the rates of proton abstraction since the reverse reaction must have a very low activation energy. Several new equations have been developed relating peak shapes to exchange rates.

A number of papers have appeared describing the application of nuclear magnetic resonance (n.m.r.) spectroscopy to the measurement of proton exchange rates.[1-6] These methods, in their simplest form, are based on one of two ideas. (1) Two distinguishable protons will give rise to two lines in n.m.r. spectra provided that the frequency with which they exchange is small by comparison with the difference between the two absorption frequencies. These lines merge if the exchange frequency is large with respect to the difference between the absorption frequencies and with intermediate exchange frequencies intermediate line shapes are predicted. (2) If a multiplet is caused by spin–spin coupling with a proton which is also exchanging the multiplet will merge to a single line if the exchange frequency is large with respect to *J*, the spin–spin coupling constant. Again, intermediate line shapes are predicted for intermediate exchange rates.

If an alkyne, R—C≡CH, is dissolved in a dilute, partially aqueous solution of hydroxide ion the exchange reaction shown in eq. 1 takes place.[7-9]

[1] H. S. Gutowsky and R. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

[2] H. M. McConnell, *ibid.*, **28**, 430 (1958).

[3] J. I. Kaplan, *ibid.*, **29**, 462 (1958).

[4] G. G. Hammes and L. E. Erickson, *J. Chem. Ed.*, **35**, 611 (1958).

[5] S. Meiboom, *Z. Elektrochem.*, **64**, 50 (1960).

[6] M. Takeda and E. O. Stejskal, *J. Am. Chem. Soc.*, **82**, 25 (1960).

[7] F. A. Long and P. Ballinger, *ibid.*, **81**, 3148 (1959).

[8] E. A. Halevi and F. A. Long, *ibid.*, **83**, 2809 (1961).

[9] H. B. Charman, G. V. D. Tiers, M. M. Kreevoy and G. Filipovich, *ibid.*, **81**, 3149 (1959).

Since the position of equilibrium for this reaction lies far to the left under the indicated conditions[10,11]

$$\mathrm{R{-}C{\equiv}C{-}H} + \mathrm{OH}^- \rightleftharpoons \mathrm{R{-}C{\equiv}C}^- + \mathrm{H_2O} \quad (1)$$

the rate determining step for exchange of the acetylenic proton with the protons of the solvent is probably the abstraction of a proton from the alkyne by hydroxide ion.

Exchange rates for a number of alkynes have now been measured by the line broadening techniques mentioned above. The solvent, in most cases, was a mixture containing 45% water by volume, about 5% acetylene, and fractional percentages of an intensity standard and sodium hydroxide. The rest of the solvent was *t*-butyl alcohol. This solvent mixture shows only one "hydroxylic proton" resonance because of the rapid exchange between the alcohol and water protons.

The work was begun using aqueous pyridine as the solvent,[9] but this solvent reacted irreversibly with several of the oxygen-containing alkynes to be studied.

Results

In cases where R has no hydrogen atoms on the carbon atom adjacent to the triple bond, only the broadening of the acetylenic proton peak is available for rate measurements. Starting with the Bloch equations as generalized by McConnell[2] to include chemical exchange and considering that the alkyne (B) and the hydroxylic solvent (A) may be present in any proportions equation 2 is obtained for the absorption mode in slow passage. (Notation is that of Bloch[12] and McConnell.[2]) height of the acetylenic resonance peak, v_B, can, therefore, be obtained by putting the conditions $\Delta\omega_B = 0$, $\Delta\omega_A = \Delta\omega$ into eq. 2. After making substitutions

$$\frac{1}{\tau_{2A}} = \frac{1}{T_{2A}} + \frac{1}{C\tau_B}$$

$$\frac{1}{\tau_{2B}} = \frac{1}{T_{2B}} + \frac{1}{\tau_B}$$

$$\tau_A = C\tau_B$$

$$C = r\cdot/n_B$$

eq. 3 is obtained. Equation 3 gives the inverse of the first-order rate constant for exchange, τ_B, in terms of the peak height and quantities which are not functions of the exchange rate. In the present cases $\tau_{2A} \sim \tau_{2B} \sim 0.5$ sec. Using this value, along with the previously given parameters and the assumption that $M_z{}^A = CM_z{}^B$ (with $C \sim 100$), it is readily shown that the terms in eq. 3 containing $\Delta\omega$ are very much larger than those that do not contain $\Delta\omega$ when $\tau_B > 0.3$ sec. By dropping the smaller terms in eq. 3, it can be simplified to eq. 4. Using the present parameters, rates calculated from eq. 4 differ by less than 0.1% from those calculated with eq. 3. Noting that τ_B is much larger than T_{2B} under conditions of slow exchange, the value $-T_{2B}M_z{}^B\omega_i$ can be obtained for the height of the unbroadened peak, $V_B{}^\infty$, from eq. 4. Substituting this value into eq. 4, τ_B is obtained entirely as a function of measurable quantities in eq. 5, since $2/T_{2B}$ is the width at half height of the appropriate peak in a non-exchanging solution.[12,13]

$$-\frac{V}{\omega_i} = \frac{\left\{M_z{}^B\left(\frac{1}{\tau_{2A}} + \frac{1}{\tau_B}\right) + M_z{}^A\left(\frac{1}{\tau_{2B}} + \frac{1}{\tau_A}\right)\right\}\left(\frac{1}{\tau_A\tau_B} - \frac{1}{\tau_{2A}\tau_{2B}} + \Delta\omega_A\Delta\omega_B\right) - (M_z{}^B\,\Delta\omega_A + M_z{}^A\Delta\omega_B)\left(\frac{\Delta\omega_B}{2A} + \frac{\Delta\omega_A}{2B}\right)}{\left(\frac{1}{\tau_A\tau_B} - \frac{1}{\tau_{2A}\tau_{2B}} + \Delta\omega_A\Delta\omega_B\right)^2 + \left(\frac{\Delta\omega_B}{\tau_{2A}} + \frac{\Delta\omega_A}{\tau_{2B}}\right)^2} \quad (2)$$

$$-\frac{V_B}{\omega_i} =$$

$$\frac{\left\{M_z{}^B\left[\frac{1}{T_{2A}} + \frac{1}{\tau_B}\left(1 + \frac{1}{C}\right)\right] + M_z{}^A\left[\frac{1}{T_{2B}} + \frac{1}{\tau_B}\left(1 + \frac{1}{C}\right)\right]\right\}\left(\frac{1}{T_{2A}T_{2B}} + \frac{1}{T_{2A}\tau_B} + \frac{1}{C\tau_B T_{2B}}\right) + M_z{}^B\,\Delta\omega^2\left(\frac{1}{T_{2B}} + \frac{1}{\tau_B}\right)}{\left(\frac{1}{T_{2A}T_{2B}} + \frac{1}{T_{2A}\tau_B} + \frac{1}{C\tau_B T_{2B}}\right)^2 \Delta\omega^2\left(\frac{1}{T_{2B}} + \frac{1}{\tau_B}\right)^2} \quad (3)$$

The approximation of slow passage

$$(\dot{\omega}_A = \dot{\omega}_B = \dot{V}_A = \dot{V}_B = \dot{M}_z{}^A = \dot{M}_z{}^B = 0)$$

is justified by the experimental observation that the results were independent of the sweep rate under the conditions used.

The resonance peak for the acetylenic protons and that for the hydroxylic protons are separated by about 400 sec.$^{-1}$ in the absence of exchange broadening ($\tau_A = \tau_B = \infty$). No measurements were made by this method when τ_B was less than 0.3 sec. By appropriate substitution in eq. 1, it can be shown that $\Delta\omega$, the frequency separation of the two peaks, should change by much less than one sec.$^{-1}$ when τ_A changes from ∞ to 0.3 sec. Experimentally no change at all was ever observed so it will be assumed in the rest of this section that the resonance frequency of the acetylenic protons, ω_B, is unchanged by exchange broadening. The

$$-V_B = \frac{T_{2B}\,\tau^B\,M_{zB}\,\omega_i}{T_{2B} + \tau_B} \quad (4)$$

$$\frac{1}{\tau_B} = \frac{V_B{}^\infty - V_B}{V_B\,T_{2B}} \quad (5)$$

In practice, it developed that neither $V_B{}^\infty$ nor T_{2B} was sufficiently reproducible to be carried over from one experiment to another. A nonexchanging reference substance with a sharp peak close to that of the acetylenic proton (methanol, dimethylsulfoxide or mesitylene was used) was, therefore, included. The required quantities in exchanging solutions are given in eqs. 6 and 7, in which quantities subscripted with R refer to the reference substance. The ratio of relaxation times can be deter-

$$V_B{}^\infty = V_R d \quad (6)$$

$$T_{2B} = -V_B/M_z{}^B\omega_i \quad (7)$$

$$d \equiv n_R T_{2B}/n_B T_{2R}$$

mined from the ratio of peak heights in the absence

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(10) J. B. Conant and G. W. Wheland, *J. Am. Chem. Soc.*, **54**, 1212 (1932).

(11) W. K. McEwen, *ibid.*, **58**, 1124 (1936).

(12) F. Bloch, *Phys. Rev.*, **70**, 460 (1946).

(13) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 97.

of exchange. The quantity $M_z\omega_i$, at constant applied frequency should be simply proportional to the number of protons giving rise to a particular peak. It is more convenient to determine $M_z\omega_i$ for simpler systems, and this was done in a straight forward fashion for tetramethylsilane, mesitylene (the methyl group) and methyl alcohol (the methyl group), all in carbon tetrachloride solution. The values, after division by proton concentration were 20.1, 20.5 and 17.0 cm. sec.$^{-1}$ at 70 db. attenuation and recorder level 200. Each of the values cited was the average of about twenty determinations with an average deviation from the mean of about 10%. In order to get values that were independent of sweep rate, it was found necessary to reduce the sweep rate until the width at half height was at least one half cm. To test the invariance of $M_z\omega_i$ under changes in instrumental conditions, it was remeasured for tetramethylsilane with a magnetic field sufficiently inhomogeneous to broaden it from 3 to 90 sec.$^{-1}$. This resulted in an increase to 25.6 cm. sec.$^{-1}$, hardly outside the combined uncertainties.

With two of the compounds studied, 3-methoxy-1-propyne and 3,3-diethoxy-1-propyne, spin-spin coupling gives rise to closely spaced multiplets for both the acetylenic proton and the 3-protons.[14] Insertion of the conditions

$$M_z{}^A = M_z{}^B \equiv M_z$$
$$T_{2A} = T_{2B} \equiv T_2$$
$$\tau_A = \tau_B \equiv \tau$$
$$\Delta\omega_A = \Delta\omega_B \equiv \delta\omega$$

into eq. 2 yields eq. 8 for V_m, the intensity of absorption midway between the peaks. In the absence of exchange τ is infinite so that $2/\tau$ and $2/T_2\,\tau$

$$-V_m = \frac{2M_z\omega_i(1/T_2 + 2/\tau)}{1/T_2{}^2 + 2/T_2\tau - \delta\omega^2} \tag{8}$$

are zero and eq. 8 simplifies to eq. 9.

$$-V_m\infty = \frac{2M_z\omega_i/T_2}{1/T_2{}^2 + \delta\omega^2} \tag{9}$$

Inserting the conditions

$$\frac{1}{\tau_{2A}} = \frac{1}{\tau_{2B}} \equiv \frac{1}{\tau_2}$$
$$M_z{}^A = M_z{}^B \equiv M_z$$
$$\Delta\omega_A = 2\delta\omega$$
$$\Delta\omega_B = 0$$
$$\tau = \infty$$

in eq. 1 gives V_p, the height of one of the broadened peaks of the doublet, as shown in eq. 10.

$$-V_p\infty = \frac{M_z\omega_i(2/T_2{}^2 + 4\delta\omega^2)}{1/T_2{}^3 + 4\delta\omega^2/T_2} \tag{10}$$

A typical value of T_2 is 0.5 sec. and a typical value of $\delta\omega$ is 8 sec.$^{-1}$. With values such as these, eq. 11, which is analogous to eq. 7, gives a good approximation to $V_p\infty$.

$$-V_p\infty = M_z\omega_i T_2 \tag{11}$$

When eqs. 9 and 11 are combined $M_z\omega_i$ can be obtained in terms of $V_p\infty$ and $V_m\infty$, as shown in eq. 12. Equation 12 provides a check on the peak

$$(M_z\omega_i)^2 = \frac{V_m\infty\, V_p\infty\, \delta\omega^2}{2 - V_m\infty/V_p\infty} \tag{12}$$

areas obtained by direct measurement. After correction to unit proton concentration the 3-proton of 3,3-diethoxy-1-propyne gave an $M_z\omega_i$ of 18.0 cm. sec.$^{-1}$, the 1-proton gave 24.3 cm. sec.$^{-1}$, and the 3-protons of 3-methoxy-1-propyne gave 17.8 cm. sec.$^{-1}$, all measured at 70 db. and recorder level 200. These are in excellent agreement with the directly measured values and all six were averaged to give 19.8 cm. sec.$^{-1}$, which was used throughout the rest of this paper. Exchange rates can now be calculated from eq. 13, which combines eqs. 5, 6 and 7.

$$1/\tau_B = \frac{M_z{}^B\omega_i(\mathrm{d}V_R - V_B)}{V_B\mathrm{d}V_R} \tag{13}$$

If eq. 1 represents the rate-determining step for exchange the quantity $1/\{\tau_B(\mathrm{OH}^-)\}$, which is k_2, the second-order rate constant for exchange, should be invariant under changes in base concentration in dilute base. Table I shows a successful test of this hypothesis for phenylacetylene in the standard solvent. Three per cent phenylacetylene was used and 0.3% dimethylsulfoxide was the reference. No significant changes in k_2 were observed for an eight fold change in the hydroxide ion concentration and the scatter is not excessive. The average value of k_2 is 43 ± 5 l. mole^{-1} sec.$^{-1}$.

TABLE I

THE RATE OF EXCHANGE OF PHENYLACETYLENE WITH HYDROXYLIC PROTONS AS A FUNCTION OF BASE CONCENTRATION

10^2 (OH$^-$)	k_2, l. mole^{-1} sec.$^{-1}$
0.878	41
1.31	30
1.76	42
2.63	42
3.51	53
5.26	41
7.02	51

In the cases where the 3-proton or protons give rise to a doublet, it was convenient to determine the exchange rate from the intensity of absorption at the midpoint of the doublet. (The single case of a higher multiplet will be discussed separately.) With exchange the doublet merges to a single line with a sharp increase in intensity at the midpoint.[1] Equation 14 gives $1/\tau$ in terms of $M_z\omega_i$, V_m and T_2. Since the two peaks of the doublet are identical, quantities identified with *A* are identical with those identified with *B* and the identifications are dropped.

$$-\frac{1}{\tau} = \frac{V_m\delta\omega^2T_2 + V_m/T_2 + 2M_z\omega_i}{4M_z\omega_iT_2 + 2V_m} \tag{14}$$

In eq. 14 $M_z\omega_i$ is the area under one of the two peaks of the doublet. The intensity due to the protons in question was assumed to be equally divided between the two peaks. In an exchanging solution T_2 was obtained from the height of a reference peak and eq. 6 and 11. The use of eq. 11 instead of eq. 10 to calculate T_2 is less well justified with 3,3-diethoxy-1-propyne than with 3-methoxy-1-propyne because $\delta\omega^2$ is smaller in the former case. To test the usefulness of eq. 11, T_2 for one of the measurements with the former compound was recalculated *via* eq. 10 and the corrected T_2 used to calculate

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[14] M. M. Kreevoy, H. B. Charman and D. R. Vinard, *J. Am. Chem. Soc.*, **83**, 1978 (1961).

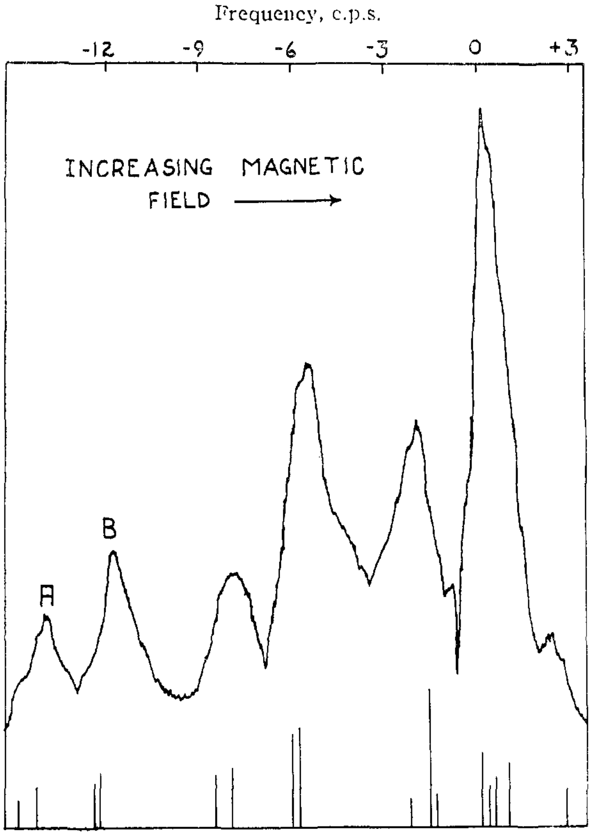

Fig. 1.—Theoretical and observed n.m.r. spectra of $HOCH_2\mathbf{CH_2}C{\equiv}\mathbf{CH}$ in the absence of base. The portion of the spectrum shown is that arising from the boldfaced protons. The rest of the spectrum is unexceptional.

k_2. The resulting k_2 was only changed from 93 to 91 l. mole^{-1} sec.$^{-1}$ so the additional labor involved in the use of eq. 10 was not thought to be justified.

In one case, 1-butyne-4-ol, a complex multiplet resulted from the interaction of the methylene protons with the acetylenic proton because the coupling constant, J_{13}, was comparable to the frequency separation of the unsplit lines, Δ_{13}. This situation was further complicated by the splitting of each peak resulting from the C_3 methylene group into a triplet by the hydrogens of the C_4 methylene group. Assuming free rotation about the single bonds two coupling constants, J_{34} and J_{13}, and two "chemical shifts," Δ_{34} and Δ_{13} are needed to analyze this spectrum. The observation of a simple triplet for the C_4 methylene group indicates that J_{14} is essentially zero. The hydroxylic proton exchanges rapidly with the hydroxylic protons of the solvent and, therefore, neither gives rise to a separate line in the spectrum nor splits the lines of the C_4 protons.

By inspection it was obvious that Δ_{34} ($\sim$500 sec.$^{-1}$) was large by comparison with J_{34} so that J_{34} could be obtained from the spacing of the C_4 methylene triplet in the usual way. It is 41 sec.$^{-1}$. To obtain J_{13} an n.m.r. spectrum of 1-butyne-4-ol was obtained in carbon tetrachloride solution. The change in solvent results in a considerable shift in the acetylenic proton peak position relative to that of the methylene protons due to changes in the hydrogen bonding of the former but does not materially alter the coupling constant.[14] In carbon tetrachloride solution J_{13} could be evaluated from the spacing of the triplet due to the acetylenic proton. It had the value 15 sec.$^{-1}$. Using the known J values and the fact that $\Delta_{34} >> J_{34}$ a series of theoretical spectra were constructed using the eqs. of Bernstein, Pople and Schneider[15] for various values of Δ_{13}, and these were compared with the observed spectrum. (The theoretical spectra are those of an AB_2 system with each of the B_2 lines split into a triplet.[15]) The best fit was obtained with a value of 7.3 sec.$^{-1}$ Theoretical and observed spectra for the C_1 and C_3 protons are compared in Fig. 1.

In basic solutions the exchange rate for 1-butyne-4-ol was obtained from the height of peak B in Fig. 1, using eq. 15.

$$\frac{1}{\tau} = \frac{-\beta + \sqrt{\beta^2 - 4\alpha\gamma}}{2\alpha} \tag{15}$$

$$\alpha \equiv \frac{4V_B}{T_2{}^2} + \Delta\omega^2 V_B + \frac{4(M_z{}^B\omega_i + M_z{}^A\omega_i)}{T_2}$$

$$\beta \equiv \frac{4V_B}{T_2{}^3} + \frac{2\Delta\omega^2 V_B}{T_2} + \frac{4(M_z{}^B\omega_i + M_z{}^A\omega_i)}{T_2{}^2}$$

$$\gamma \equiv \frac{V_B}{T_2{}^4} + \frac{\Delta\omega^2 V_B}{T_2{}^2} + \frac{M_z{}^B\omega_i + M_z{}^A\omega_i}{T_2{}^3} + \frac{M_z{}^B\omega_i\Delta\omega^2}{T_2}$$

Peak B is merging with peak A as the exchange becomes more rapid. Equation 15 was obtained from eq. 3 by inserting the conditions

$$T_{2A} = T_{2B} \equiv T_2$$
$$\tau_B = \tau_A \equiv \tau$$
$$C \equiv 1$$

and solving for $1/\tau$ in straightforward fashion. (It was not evident by inspection, but the answers finally obtained from eq. 15 were only a few per cent. different from those obtained from eq. 13.) The required values of $M_z{}^A\omega_i$ and $M_z{}^B\omega_i$ were obtained from the previously determined value of $M_z\omega_i$ at unit concentration and the theoretical relative intensities of peaks A and B.[15] Equations 6 and 7 and the height of a reference peak gave T_2 for exchange-broadened peaks. The parameter d previously had been determined in neutral solutions. (The quantity "d" no longer has its original significance because only a fraction of the intensity due to the C_2 methylene group is in the peak B but d is still given by eq. 6.)

Second order rate constants accumulated by these various methods for solutions at 24 ± 3° are shown in Table II.

TABLE II

R	k_2, l. mole^{-1} sec.$^{-1}$	Ave. dev.	Eq. used	σ^*
$HOCH_2CH_2$	8.9	1.3	9	0.20
$HOC(CH_3)_2$	34	3	5	.37
$CH_3OC(CH_3)_2$	43	7	5	.46
CH_3OCH_2	99	30	13	.65
$(C_2H_5O)_2CH$	96	16	13	1.3
C_6H_5	43	2	5	0.600
C_6H_5	1200[a]			
C_6H_5	460[b]			

[a] In a solvent containing 15% water and 73% pyridine; ref. 9. [b] In pure water, neglecting an isotope effect, ref. 8.

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(15) H. J. Bernstein, J. A. Pople and W. G. Schneider, *Can. J. Chem.*, **35**, 65 (1957).

Except where otherwise noted, the solutions contained 45% water by volume and were made up as described above. Several values in other solvents are included for comparison and for use in the discussion section.

Discussion

The inductive parameter, σ^*,[16] for each of the substituents, is listed in Table II along with the rate constants. Unfortunately, of the present substituents, directly determined σ^* values are available only for the phenyl and the methoxymethyl groups, and the preferred value for the latter in hydroxylic solvents (0.65)[17] is somewhat different from that originally proposed (0.52).[16] However, a number of fairly reliable methods are available for estimating new σ^*'s from known values.[16] Sigma star for $HOCH_2CH_2$ was obtained from that for $HOCH_2$, 0.56, by dividing by 2.8, the standard factor for the introduction of a methylene group. For $HOC(CH_3)_2$, 0.56 was added to -0.19, the σ^* for the isopropyl group. This involves the assumption that the addition of two methyl groups to a hydroxymethyl group has the same effect on the σ^* of the hydroxymethyl group as the addition of two methyl groups to an original methyl group has on the σ^* of the original methyl group.[16] The σ^* for $CH_3OC(CH_3)_2$ was obtained in the same way as that for $HOC(CH_3)_2$. The σ^* for $(C_2H_5O)_2CH$ was obtained by doubling that for a methoxymethyl group and is undoubtedly somewhat too large.[16]

Figure 2 shows a plot of log k_2 *vs.* σ^*. It is plain that a straight line of acceptable precision is defined by four of the saturated substituents. The point for the diethoxymethyl substituent falls below the line by an amount which seems to be outside the combined uncertainty in the rate constant and the σ^* value. This deviation may be due to the consumption of base by the reaction shown in eq. 16. This would be

$$OH^- + (C_2H_5O)_2CHC{\equiv}CH \rightleftarrows HOH + (C_2H_5O)_2\overline{C}{-}C{\equiv}CH \quad (16)$$

facilitated by the presence of the two electronegative oxygen atoms in addition to the acetylenic group. Because the acetylene was present in large excess, the hydroxide ion concentration and, thus, the rate, would still be proportional to the concentration of sodium hydroxide originally added. The organic anion would be very ineffective in catalyzing exchange because of its bulk and because the reaction shows very little general base catalysis.[8,9] The reaction shown in eq. 16 would not contribute to the broadening of the n.m.r. lines because it would be slow (because of nonbonded atom repulsions in the transition state) although relatively complete. Alternatively the failure of the diethoxymethyl substituent to correlate may be due to the presence of traces of ethyl formate, possibly introduced in preparing the acetal from the aldehyde. Ethyl formate would also consume the base, producing the relatively non-catalytic formate ion.

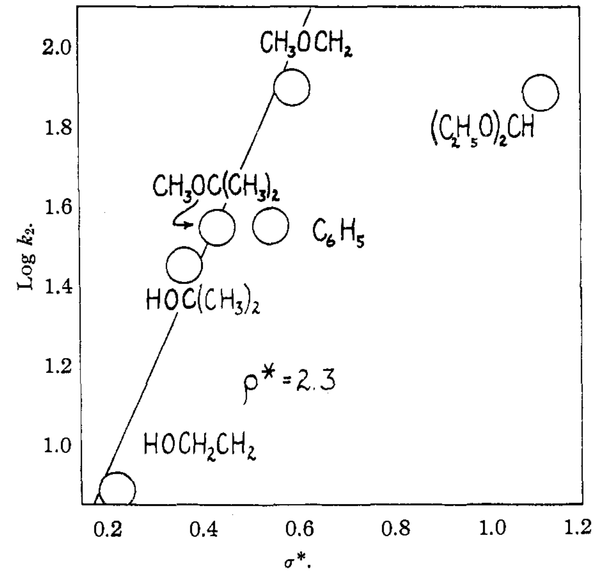

Fig. 2.—A plot of log k_2 for base catalyzed proton exchange *vs.* the Taft σ^*'s. The substituents are indicated with each point.

The correlation line for the other four saturated substituents has a slope, ρ^*, of 2.3, assigned by inspection. This would not be changed if the phenylacetylene point were included. Unfortunately, the total spread in rates is only a little over a power of ten so no great precision can be attributed to ρ^*, but Fig. 2 suggests that its value is not uncertain by more than ± 0.2.

A priori it is not likely that the reaction shown in eq. 1 going from right to left is subject to very much free energy of activation. Eigen and coworkers have shown that the reaction of the hydronium ion with hydroxide ion[18] and fluoride ion[19] occur at essentially the diffusion controlled rate, and even the large nitrophenolate ions react with hydronium ion at a rate close to that limit.[19] Energy of activation arises largely from repulsions between non-bonded atoms.[20] If alkyd ion and a water molecule approach each other with the two carbon atoms, the hydrogen atom, and the oxygen atom colinear the increase in non-bonded repulsions should be negligible because a hydrogen bond would form at intermediate internuclear distances. There should be a negative entropy of activation (and, thereby, a positive free energy of activation) because of the immobilization of the water molecule which is transferring the proton to the alkyd ion. This approach is essentially equivalent to considering that some collisions will be ineffective because the water molecules will be improperly oriented. The orientation of the alkyd ion is not considered because it must be properly oriented for one water molecule or another at any time. An upper limit on this would be the total molar entropy of liquid water, which is 17 cal. mole^{-1} deg.$^{-1}$. In addition, the required solvent rearrangement accompanying the proton transfer may contribute small incre-

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[16] R. W. Taft, in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chap. 13.

[17] R. W. Taft, private communication.

[18] M. Eigen and L. De Maeyer, *Z. Elektrochem.*, **59**, 986 (1955).

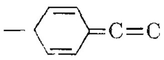
[19] M. Eigen and K. Kustin, *J. Am. Chem. Soc.*, **82**, 5963 (1960).

[20] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 77.

ments to both the entropy and enthalpy of activation. If the upper limit is taken as the correct value for the water immobilization effect and the solvent rearrangement effect is neglected, the $\Delta F_{25}^{\ddagger}$ for the reaction shown in eq. 1 going from right to left is predicted to be 5.5 kcal. mole^{-1} in pure water. The rate constant for this reaction has been shown experimentally to be $\backsim 10^8$ l. mole^{-1} sec.$^{-1}$[8] which gives a $\Delta F^{\ddagger}$ of 4.4 kcal. mole^{-1} when liquid water is taken as the standard state. Considering the roughness of the entire calculation, this is entirely acceptable agreement with the theoretically estimated value. From the success of such a model it can be concluded that the relative equilibrium constants for reactions such as that shown in eq. 1 are governed entirely by relative rate constants such as those shown in Table II, and the ρ^* evaluated above pertains to the equilibrium constants as well as the rate constants for this reaction.

The value of ρ^* obtained is very suitable for such equilibrium constants. It is somewhat larger than the values obtained for the ionization of aliphatic carboxylic acids, RCOOH (1.7)[16] and alcohols, RCH_2OH (1.4)[21] and considerably smaller than ρ^* for ionization of mercaptans, RSH (3.4)[22] in water. If the present reaction had been studied in pure water, ρ^* probably would have been even closer to the former values.[23] This is in accord with the view that the transmission of inductive effects through a triple bond is only a little more efficient than their transmission through a single bond (and less efficient than their transmission through a double bond.)[24,25]

The point for phenylacetylene was not used in evaluating ρ^* because of the possibility that the unsaturated group might influence the proton abstraction rate in a non-inductive manner. Delocalization of the charge through resonance from such as is prohibited in first approximation because the unshared pair of electrons occupy an oribital orthogonal to the π orbitals of the conjugated system. Nevertheless, the resonance energy of the conjugated system might be altered by the change in the coulomb integral of the terminal carbon atom on abstraction of the proton. In fact, the point for phenylacetylene misses the correlation line by only 0.3 log unit, so any such effect must be small. This provides direct experimental support for the frequently used approximation that changes in coulomb integrals have a relatively small effect on resonance energies.[26]



Experimental

The n.m.r. spectra were produced with a Varian Model 4311 high resolution spectrometer operating at 56.442 cy./sec. Most of the spectra were produced at attenuation 70 db. and recorder level 200. Relative frequencies were established by the side-band technique. The side-band frequencies were counted with a Hewlett–Packard counter. Most spectra were obtained with a sweep rate of $\sim$3 cy. sec.$^{-1}$ sec.$^{-1}$, but those used in measuring $M_z\omega_1$ were obtained with a sweep rate of $\sim$0.3 cy. sec.$^{-1}$ sec.$^{-1}$ Each intensity used to determine a rate constant was the average of about four determinations. Operating temperatures could not be controlled precisely but were measured and recorded at the time spectra were made.

The preparation and purification of the alkynes has been reported previously.[14] *tert*-Butyl alcohol was dried over calcium oxide and distilled through a 48-cm. metal gauze column. The central 60% had appropriate physical constants and was used. Carbonate free sodium hydroxide was prepared and standardized in the usual way. All solutions were protected from atmospheric carbon dioxide by streams of carbon dioxide-free nitrogen during preparation. Solutions made up in this way gave no precipitate with barium chloride.

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[26] R. A. Mulliken, C. A. Rieke and W. G. Brown, *ibid.*, **63**, 41 (1941).