cyanoacetylene is highly unstable in the concentrated basic solutions which would be required.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their financial support of this research.

Supplementary Material Available: Table S1 (6 pages) of rate data; ordering information is given on any current masthead page.

General Base Catalyzed Hydrogen Exchange of 1-Octyne, 4-Nitrophenylacetylene, and 3-(Phenyldimethylammonio)-1-propyne. Brønsted Relations and Normal Acid Behavior

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Rates of loss of tritium from the title compounds labeled at the acetylenic hydrogen position were measured in aqueous primary amine buffer solutions at 25 °C. These data give Brønsted relations with essentially unit exponents: $\beta = 0.97 \pm 0.06$ for 1-octyne, $\beta = 0.97 \pm 0.05$ for 4-nitrophenylacetylene, and $\beta = 0.98 \pm 0.05$ for 3-(phenyldimethylammonio)-1-propyne, which indicates that these acetylenes are "normal" rather than pseudo carbon acids.

Proton transfers to and from carbon are generally intrinsically slow processes, in contrast to the very rapid proton-transfer reactions of "normal", i.e., oxygen and nitrogen, acids and bases.[1] One of the factors believed to be responsible for this difference is the presence of localized electron pairs at the proton-accepting sites of normal bases; the proton-accepting electron pairs of carbon bases which protonate slowly, on the other hand, are strongly delocalized.

It follows from this idea that carbon bases with localized electron pairs might be protonated rapidly and that such bases and their conjugate acids might, therefore, show normal acid-base behavior. We have recently found support for this hypothesis in the nature of the Brønsted relations for detritiation of phenylacetylene and chloroform catalyzed by a series of amine bases.[2] These hydrogen-exchange processes occur via thermodynamically uphill acid-base reactions, eq 1, which generate carbanions, 1 and

$$\mathrm{RT} + \mathrm{B} \rightarrow \mathrm{R}^- + \mathrm{BT}^+ \qquad (1)$$

2, whose basic electron pairs are formally localized on single

$\mathrm{PhC{\equiv}C{:}^-}$ (1) $\quad$ $\mathrm{Cl_3C{:}^-}$ (2)

atoms. The Brønsted relations for these reactions have unit exponents ($\beta = 1$), just like those for uphill proton transfers from normal oxygen and nitrogen acids to normal oxygen and nitrogen bases. Brønsted exponents for carbon-acid/normal-base reactions which generate delocalized carbanions, on the other hand, are invariably less than unity.

In order to determine just how general this phenomenon is, we have examined the detritiation of other acetylenes. In this paper we report our results for 4-nitrophenylacetylene, 3, 1-octyne, 4, and 3-(phenyldimethylammonio)-1-propyne, 5.

$\mathrm{4\text{-}NO_2C_6H_4C{\equiv}CH}$ (3) $\quad$ $\mathrm{C_6H_{13}C{\equiv}CH}$ (4) $\quad$ $\mathrm{PhN^+(CH_3)_2CH_2C{\equiv}CH}$ (5)

Experimental Section

Materials. 3-(Phenyldimethylammonio)-1-propyne was prepared as its bromide salt by the reaction of propargyl bromide with *N,N*-dimethylaniline.[3] 1-Octyne was purchased commercially (ICN Pharmaceuticals) and 4-nitrophenylacetylene was a gift from Professor K. Yates. These acetylenes were tritiated by exchange with tritiated water in dioxane solution by using sodium hydroxide as a basic catalyst. The site of isotopic labeling was verified by doing parallel experiments with D_2O and examining the exchanged material by proton NMR. Tritiated substrates for kinetic determinations were purified by distillation and recrystallization, and their purity was checked by gas chromatography.

Kinetics. Detritiation reactions of 4-nitrophenylacetylene and 3-(phenyldimethylammonio)-1-propyne were conducted in stoppered flasks immersed in a constant-temperature bath operating at 25.0 ± 0.02 °C. 1-Octyne, however, was too volatile to be handled in this way; it partitioned between the vapor and solution phases and, when the flask was opened for sampling, sufficient octyne escaped to give poor kinetic results. Individual portions of reaction mixtures of this acetylene were, therefore, contained in the constant-temperature bath in screw-cap vials; when these vials were filled, care was taken to leave as little vapor space as possible in order to minimize substrate partitioning.

Samples of reaction mixtures were taken by removing 5-mL aliquots from the reaction flasks or individual vials by pipet and then immediately quenching these by addition to an excess of aqueous acid. The quenched solutions were subsequently extracted with accurately pipetted 15-mL portions of toluene, the toluene extracts were dried with anhydrous calcium chloride, and 10-mL aliquots of the dried solutions were added to 10-mL portions of toluene-based counting solution (8 g of 2,5-diphenyloxazole plus 0.1 g of 1,4-bis[2-(5-phenyloxazoyl)]benzene per liter). These solutions were then assayed for radioactivity by using a Packard 314 EX liquid scintillation counter; data were collected for a sufficiently long time to ensure good counting statistics (at least 10^5 counts).

The ionic amine 3-(phenyldimethylammonio)-1-propyne could not be extracted from quenched aqueous solution by toluene in

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Table I. Summary of General Base Catalytic Coefficients for Detritiation of Acetylenes in Aqueous Solution at 25 °C[a]

		$k_B/10^{-3}$ M^{-1} s^{-1}		
base	pK_a(BH^+)	C_6H_{13}-C≡CT	4-$NO_2C_6H_4$-C≡CT	$C_6H_5N^+$-$(CH_3)_2$-CH_2C≡CT
$CH_3(CH_2)_3NH_2$	10.60[b]	24.9		
$CH_3O(CH_2)_3NH_2$	9.92[c]	3.57		
$C_6H_5CH_2NH_2$	9.35[d]	0.523	145	340
$(CH_3O)_2CHCH_2NH_2$	8.54[e]	0.0971	8.32	32.2
$(CH_2OH)_3CNH_2$	8.07[f]	0.121	7.81	26.2
$CNCH_2CH_2NH_2$	7.80[g]	0.0389	4.51	5.03
$CF_3CH_2NH_2$	5.59[e]	0.000226	0.0214	0.0771
$CNCH_2NH_2$	5.34[h]		0.0157	0.0273
HO^-	15.74	1.69×10^4	8.30×10^5	2.05×10^6

[a] Ionic strength maintained at 0.10 M through the addition of NaCl. [b] Evans, A. G.; Haman, S. D. *Trans. Faraday Soc.* **1951**, *47*, 34–40. [c] Love, P.; Cohen, R. B.; Taft, R. W. *J. Am. Chem. Soc.* **1968**, *90*, 2455–2462. [d] Robinson, R. A.; Kiang, A. K. *Trans. Faraday Soc.* **1956**, *52*, 327–331. [e] Reference 2. [f] Datta, S. P.; Grzybowska, A. K.; Weston, B. A. *J. Chem. Soc.* **1963**, 792–796. [g] pK_a (29 °C) = 7.7 (Soloway, S. S.; Lipschitz, H. *J. Org. Chem.* **1958**, *23*, 613–615) adjusted to 25 °C using $-d(pK_a)/dT = (pK_a - 0.9)/T$ (Perrin, D. D. *Aust. J. Chem.* **1964**, *17*, 484–488). [h] Stevenson, G. W.; Williams, D. *J. Am. Chem. Soc.* **1958**, *80*, 5943–5947.

this way, and it was, therefore, separated from water by vacuum evaporation. In this technique, aliquots of reaction mixture were quenched by addition to acid contained in 100-mL round-bottomed flasks; these were then attached to a high vacuum line, and water was removed with the aid of gentle heating (30 °C). The residues were then taken up in standard volumes of 10:1 dioxane–water, and 5-mL portions of the resulting solutions were combined with 15 mL of Bray's counting solution.[4] Radioactivity assays were conducted by liquid scintillation counting as for the toluene-based solutions.

Nine samples spaced at appropriate time intervals were generally taken per kinetic run. The data conformed to the first-order rate law well, and observed first-order rate constants were evaluated by least-squares analysis as slopes of plots of ln CPM vs. time (CPM = counts per minute corrected for background radioactivity).

Results

Kinetics. First-order rate constants for the loss of tritium from the acetylenic hydrogen position of the three substrates, **3**–**5**, were measured in wholly aqueous buffer solutions of a number of primary amines. Series of solutions of constant buffer ratio and constant ionic strength (μ = 0.10 M) but changing buffer concentration were used. Buffer concentrations were varied by factors of 5–10, and 4 or 5 concentrations were employed to make up a series. The results are summarized in Tables S1–S3.[5]

General-base catalytic coefficients, k_B, were evaluated from these data by analysis based on the rate law of eq 2.

$$k_{obsd} = k_{HO^-}[HO^-] + k_B[B] \tag{2}$$

In a given series of buffer solutions such as those used here, the hydroxide ion concentration generally remains sufficiently constant to make the first term of this rate law essentially invariant, and observed first-order rate constants should, therefore, increase linearly with increasing buffer base concentration. This was found to be the case here, and the data were, therefore, treated by linear least-squares methods. In buffer solutions of the two strongest amine bases used, however, hydrolysis of the bases occurred to significantly different extents at different buffer concentrations, and hydroxide ion concentrations consequently dropped somewhat as buffer concentrations were lowered. This "buffer failure" was handled as before[2] by adjusting observed first-order rate constants to values expected for a common hydroxide ion concentration. These adjustments were in all cases minor and never changed k_{obsd} by more than 4%. The general base catalytic coefficients obtained in this way are summarized in Table I.

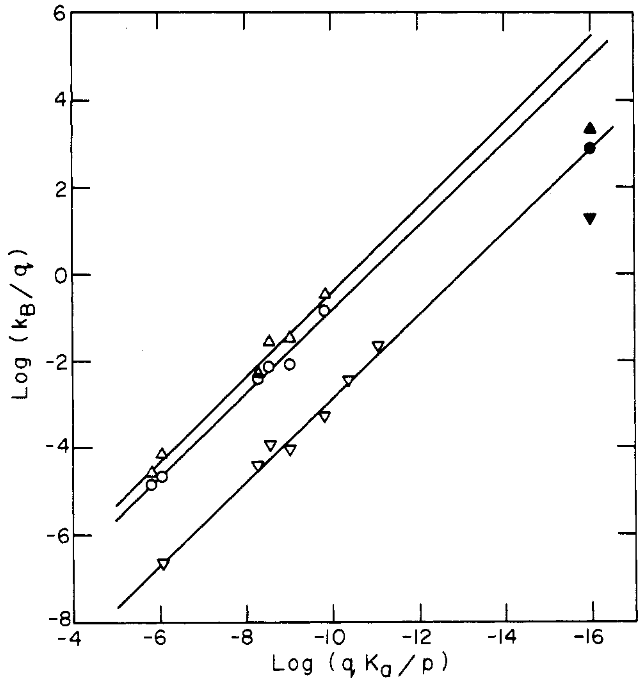

Figure 1. Brønsted relations for the detritiation of 1-octyne (▽), 4-nitrophenylacetylene (○), and 3-(phenyldimethylammonio)-1-propyne (△); filled symbols represent catalysis by hydroxide ion.

The rates of loss of tritium from the acetylenes investigated here were too rapid to allow measurement of hydroxide ion catalytic coefficients, k_{HO^-}, directly in alkali metal hydroxide solutions. Values of k_{HO^-} were, therefore, determined from the intercepts, $k_{HO^-}[HO^-]$, obtained from least-squares fitting of the data to eq 2. Hydroxide-ion concentrations needed for this purpose were obtained by calculation using literature values of thermodynamic dissociation constants of the amine conjugate acids (Table I) and activity coefficients either recommended by Bates[6] or, in the case of amine conjugate acids, estimated by the Debye–Huckel equation with an ion-size parameter of 6 Å.[7] The six or seven values of k_{HO^-} for each acetylene obtained in this way were always in good agreement with each other; the individual values are listed in Tables S1–S3,[5] and numerical averages are given in Table I.

Brønsted Relations. These general-base catalytic coefficients were used to construct the Brønsted relations shown in Figure 1. Statistical factors p = 3 and q = 1 were employed to conform with previous practice for phenylacetylene;[2] however, since all of the present catalysts were of a single type (primary amines), use of a different convention, e.g., p = 1, would not have changed the Brønsted exponents obtained. Linear least-squares analysis gave the following results: for 1-octyne, $\log (k_B/q) = -12.479 \pm 0.535 - (0.965 \pm 0.058) \log (qK_a/p)$; for 4-nitrophenylacetylene, $\log (k_B/q) = -10.475 \pm 0.437 - (0.967 \pm 0.054) \log (qK_a/p)$; and for 3-(phenyldimethylammonio)-1-propyne, $\log (k_B/q)$

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(5) Supplementary material; see paragraph at the end of this paper.

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$= -10.177 \pm 0.430 - (0.979 \pm 0.053) \log (qK_a/p)$.

In our previous study of the detritiation of phenylacetylene,[2] we found the catalytic coefficient for tris(hydroxymethyl)methylamine to be above the Brønsted correlation line for other primary amines. The same is true of each of the acetylenes examined here, but, since the present deviations (25–130%) are no greater than those for some other amines, the catalytic coefficients for tris(hydroxymethyl)methylamine were included in these correlations. The hydroxide-ion points, on the other hand, deviate much more strongly, in the opposite direction, by factors ranging from 63 to 160. Such behavior is typical of proton transfer from carbon,[2,8] and, if it were not for these large negative deviations, hydroxide-ion catalysis would have overwhelmed reaction through the amine bases, and general base catalytic coefficients could not have been determined.

Discussion

The hydrogen-exchange reactions of all three of the acetylenic substrates investigated here give Brønsted relations whose exponents are experimentally indistinguishable from unity. This is similar to the behavior we found before for hydrogen exchange in phenylacetylene and chloroform,[2] and it is similar as well to that expected for uphill proton transfer between normal acids and bases. It suggests that these acetylenes are in fact normal carbon acids.

Uphill reactions between normal acids and bases such as these have unit Brønsted exponents because the proton-transfer stage, eq 3, of the overall proton-transfer process, eq 3 and 4, is complete before the rate-determining

$$\mathrm{RH} + \mathrm{B} \rightleftarrows \mathrm{R^-{\cdot}HB^+} \tag{3}$$

$$\mathrm{R^-{\cdot}HB^+} \rightarrow \mathrm{R^-} + \mathrm{HB^+} \tag{4}$$

step; in these reactions, diffusional separation of the proton transfer products, eq 4, is rate-determining. This is in contrast to proton transfer from pseudo (carbon) acids to normal bases, where, except in the extreme thermodynamically uphill limit, the proton transfer step of the overall process is rate-determining; such reactions give Brønsted relations with less than unit exponents which reflect the symmetry of the proton-transfer transition state.[9]

It is instructive to compare the present experimentally determined Brønsted exponents with values expected if the substrates examined were acting as pseudo rather than normal acids and proton transfer rather than diffusional separation were the rate-determining step. This may be done with the aid of certain relationships between Brønsted exponents and reaction energetics, such as that provided by Marcus rate theory.[8,10] This theory expresses the Brønsted exponent β for a proton-transfer reaction step in terms of its free energy of activation, $\Delta G^\ddagger$, and its free energy of reaction, ΔG°, as in eq 5. Table II shows the

$$\beta = (\Delta G^\ddagger/\Delta G^\circ) - [(\Delta G^\ddagger/\Delta G^\circ)^2 - (\Delta G^\ddagger/\Delta G^\circ)]^{1/2} \tag{5}$$

results of calculations made by this equation using values of $\Delta G^\ddagger$ for the detritiation reactions catalyzed by a hypothetical base with $\log (qK_a/p) = -8.00$, which corresponds to the midpoint of the range of catalysts used, and values of ΔG° estimated from these $\Delta G^\ddagger$'s plus the minimum barrier for the reverse reaction (= 5.7 kcal mol^{-1})[2] consistent with a rate-determining proton-transfer mechanism. It may be seen that these predicted β's are all much less than observed values, just as was the case with the predicted value we obtained before in the same way for phenylacetylene.[2] This lack of correspondence between observed and predicted Brønsted exponents indicates that the basis on which the predictions were made, namely, that the substrates are pseudo acids, is incorrect; this provides additional support for the conclusion that they are in fact normal acids.

Table II. Comparison of Observed Brønsted Exponents with Values Predicted for Pseudo-Acid Behavior

	β		
		predicted[a]	
substrate	observed	Marcus	Lewis–More O'Ferrall
$CH_3(CH_2)_5C{\equiv}CH$	0.97 ± 0.06	0.67	0.81
$4\text{-}NO_2C_6H_4C{\equiv}CH$	0.97 ± 0.05	0.66	0.79
$C_6H_5N^+(CH_3)_2CH_2C{\equiv}CH$	0.98 ± 0.05	0.66	0.78
$C_6H_5C{\equiv}CH$[b]	0.99 ± 0.05	0.66	0.79

[a] Upper limits. [b] From ref 2.

Marcus rate theory has the unrealistic feature of being applicable over only a limited range of ΔG°, and an alternative theory without this drawback was recently proposed by Lewis and More O'Ferrall.[11] This new theory leads to an expression for β, eq 6, which is somewhat

$$\beta = 1/(2 - \Delta G^\circ/\Delta G^\ddagger) \tag{6}$$

different from the Marcus theory relationships of eq 5. Calculations were, therefore, also made with eq 6, and the results are shown in Table II. Once again there is no correspondence between predicted and observed values of β, and Lewis–More O'Ferrall rate theory, therefore, also supports the conclusion that these acetylenes are normal carbon acids.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their financial support of this work.

Supplementary Material Available: Tables S1–S3 of rate data (9 pages); ordering information is given on any current masthead page.

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