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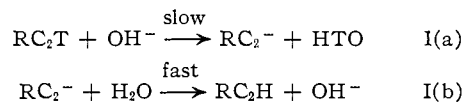
The Base Catalyzed Exchange of Phenylacetylene- t_1 in Aqueous Solution¹BY E. A. HALEVI² AND F. A. LONG

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The rate of exchange of the active hydrogen of phenylacetylene has been studied in aqueous solutions at 25° using tritium labeling. The reaction with hydroxide ion is first order in base, the rate coefficient being 2.7×10^3 l. mole⁻¹ sec.⁻¹. Comparison studies for the solvents deuterium oxide and water lead to a ratio of second order rate coefficients of $k_{OD^-}/k_{OH^-} = 1.34$, about as expected for the postulated one-step slow proton transfer mechanism. Experiments with aqueous buffers of tris-(hydroxymethyl)-amine, of 2,6-lutidine and of ammonia give evidence that the reaction is catalyzed by general bases but, relative to hydroxide ion, the contribution of the weaker bases to the rate is not so large as to make the evidence conclusive. The "uncatalyzed" exchange was searched for but not detected indicating that the proton transfer to water as a base cannot have a rate coefficient larger than about 2×10^{-10} l. mole⁻¹ sec.⁻¹. The kinetics for base catalysis, when combined with information on the acid dissociation constant of phenylacetylene, indicate that the rate coefficient for proton transfer from the acid water to the phenylacetylene anion is of the order of 10^8 l. mole⁻¹ sec.⁻¹ and that the value for the similar reaction with hydronium ion is probably around 10^{11} . The exchange has also been measured with the tritium label in the water and the same exchange rate coefficient was observed as in the forward direction, the value being associated in both cases with the rate of rupture of the carbon-tritium bond.

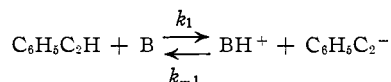
An earlier communication reported briefly on the exchange of liquid phenylacetylene- d_1 , $C_6H_5C_2D$, with the hydrogens of aqueous buffer solutions.³ The data for the two-phase system showed that the reaction was catalyzed by hydroxide ion and that the slow step very probably occurred in the aqueous phase, but the analytical method did not give sufficiently high accuracy to permit a study of general base catalysis. The present communication gives the results of a more detailed investigation. The use of tritium labeling has permitted both increased accuracy and the use of a homogeneous aqueous phase for the study.

About the only reasonable mechanism for base catalyzed exchange involves direct attack of the acetylenic hydrogen by a base



Since other bases than hydroxide ion would be expected to react similarly, this mechanism predicts general base catalysis. Essentially the same mechanism is involved in the base catalyzed enolization of ketones and the neutralization of nitroparaffins and for both of these cases general base catalysis is observed.⁴ However, the acetylene reaction might conceivably show somewhat different characteristics partly because of the simple hydrocarbon nature of the substrate, partly because of the relatively low acidity of the acetylenes and it is thus of particular interest to search for general catalysis.

The use of tritium as a label for these exchange studies offers a significant advantage beyond the obvious ones of increased ease and precision of measurement. To show this, let us consider the slow steps for both the labeled and unlabeled substrate

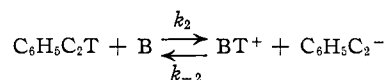


(1) Work supported by a grant from the Atomic Energy Commission.

(2) Department of Chemistry, Technion, Haifa, Israel.

(3) P. Ballinger and F. A. Long, *J. Am. Chem. Soc.*, **81**, 3148 (1959).

(4) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, gives references for these studies and summarizes the results.



When B is hydroxide ion the general rate equation is⁵

$$\frac{d[C_6H_5C_2T]}{dt} = \frac{k_2["C_6H_5C_2H"]}{1 - \beta \frac{k_{-1} - k_{-2}}{k_{-1}}} [\epsilon(1 - \alpha)\beta - (1 - \beta)\alpha] \quad (1)$$

where [" $C_6H_5C_2H$ "] is total concentration of phenylacetylene, α and β are the atom fractions of tritium in the phenylacetylene and in the water, respectively, and ϵ is the fractionation factor between substrate and water, defined as

$$\epsilon = \frac{(1 - \beta_\infty)\alpha_\infty}{(1 - \alpha_\infty)\beta_\infty}$$

The fact that tritium is present at tracer level permits some simplifications. Thus both β and α are much less than unity and [" $C_6H_5C_2H$ "] is virtually equal to [$C_6H_5C_2H$]. Similarly [$C_6H_5C_2T$] \simeq $\alpha[C_6H_5C_2H]$ and $\epsilon \simeq \alpha_\infty/\beta_\infty$. As a result the above rate equation simplifies to

$$\frac{d\alpha}{dt} = k_2(\epsilon\beta - \alpha) \quad (2)$$

which can also be written⁵ as

$$\frac{d(\alpha_\infty - \alpha)}{dt} = k_2 \frac{["C_6H_5C_2H"] + 2["H_2O"]}{2["H_2O"]} (\alpha_\infty - \alpha) \quad (3)$$

Remembering that total phenylacetylene is small compared to the total amount of water and that α is proportional to the net observed count per minute per aliquot, we obtain

$$\frac{d \ln(C_\infty - C)}{dt} = -k_2 \quad (4)$$

where C and C_∞ are the observed counts per aliquot at times t and infinity, respectively. It follows for this tracer level situation that, whether the tritium labeling is initially in the phenylacetylene or in the water, the slope of a logarithmic plot of $(C_\infty - C)$ versus time will always yield k_2 , the rate of rupture of the carbon-tritium bond by the base involved. When the isotopic indicator is used at higher than tracer level, the situation becomes distinctly more

(5) C. A. Bunton, D. P. Craig and E. A. Halevi, *Trans. Faraday Soc.*, **51**, 196 (1955).

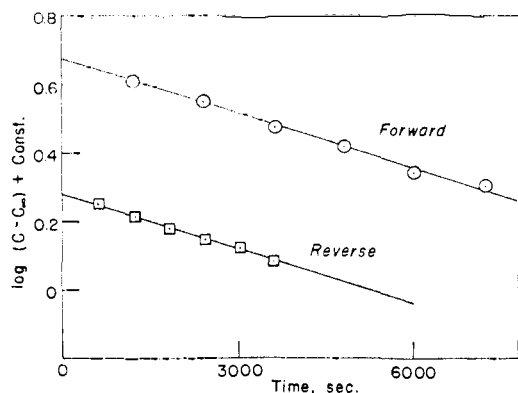


Fig. 1.—Illustrative plots for exchange kinetics. Buffer is 2,6-lutidine with $[B] = 0.1 M$, $[BH^+] = 0.02 M$, $[HCl] = 0.08 M$. \odot , $\log(C - C_\infty) - 3$ for experiments with tritium labelled phenylacetylene; \square , $\log(C - C_\infty) - 2,3$ for experiments with tritium labelled water.

complicated. Thus tritium labeling in this system permits a check of the prediction that the rate is indeed independent of the position of the label.⁶

Experimental

Isotopic Materials.—Tritiated water of strength 1 curie/gram was diluted 1:500 to a stock solution of nominally 4×10^9 disintegrations per minute per gram.

Tritiated Phenylacetylene.—Five cc. of stock tritiated water were further diluted with 20 cc. of 0.5 M sodium carbonate solution. To this was added 5 g. of phenylacetylene and the mixture was shaken in a sealed ampoule overnight. The layers were separated and the aqueous layer acidified and washed with ether. The combined organic layers were dried on calcium chloride and the ether removed *in vacuo*. The tritiated phenylacetylene was distilled at 130° in a gentle stream of nitrogen at atmospheric pressure.

99.5% deuterium oxide was used directly.

Reagents.—Phenylacetylene was distilled as described above for the labelled compound. All other reagents were analytical reagent grade materials and were used as supplied except that solid materials were dried before use.

Kinetic Procedures.—Most of the runs were carried out with labelled phenylacetylene (always present as a concentration not larger than one-fourth saturated) and unlabelled water. In each of these runs, 10–20 mg. of tritiated phenylacetylene were introduced into 100 ml. of the appropriate aqueous buffer solution in a flask fitted with an automatic pipette and kept in a thermostat at $25.0 \pm 0.02^\circ$. After complete solution of the phenylacetylene was assured, 10 cc. aliquots were run at fixed intervals into 60 ml. separatory funnels containing 5 ml. of toluene and 5 ml. of a hydrochloric acid solution sufficiently strong to neutralize all the base present. The funnel was shaken by hand and the aqueous layer run off. (Preliminary experiments indicated that the single extraction removed 98% of the phenylacetylene.) The toluene solution, together with a further 2 ml. of toluene with which the funnel was rinsed, was poured into 5 ml. of standard phosphor solution (4 g. PPO and 0.1 g. POPOP in one liter of toluene). The samples were stored for 1 hr. in the freezer of a Packard Tri-Carb Scintillation Spectrometer Model 314-DC and counted. A counting period of 5 minutes was generally enough (10000 counts or more) to reduce statistical counting error to less than 1%. An “infinity” point was taken after ten half lives and the rate constant was determined from the least-squares straight line of a plot of $\log(C - C_0)$ against time. A typical plot is shown in Fig. 1.

In reverse runs, the solutions were made up to include 5 cc. of stock tritiated water in 250 cc., and unlabelled phenylacetylene was added as above. The extraction procedure was the same as above, except that the toluene extract was

(6) A rather different but also useful reason for utilizing tritium labeling is that the reaction can be studied in the solvent D_2O as well as in H_2O . This permits comparison, for example, of the relative catalytic effectiveness of the bases OH^- (in H_2O) and OD^- (in D_2O).

washed successively three times with 0.02 M HCl. Since in these runs the samples were low in tritium, the counting period was extended to 10 minutes. Still, the statistical counting error was larger than in the direct runs, but better than 3%. A sample plot of a reverse run under conditions similar to those of the forward run is included in Fig. 1.

The error limits which are listed for rate coefficients in the various tables are simply the standard deviations from the average. These were generally less than 5%, the experiments with Tris being somewhat less good than the others, presumably because of extraction difficulties.

The calculated hydroxide ion concentration in the solutions was taken as correct, but pH readings were taken systematically with a glass electrode pH meter to guard against gross error.

Equilibrium Measurements.—The principle difficulty in equilibrium measurements was counting phenylacetylene and water under identical conditions. Water required solubilization with a small amount of alcohol, and this reduced the count somewhat by quenching. The counting of extracted phenylacetylene, as indicated above, was carried out in moist toluene. The calibration procedure adopted was to count a weighed sample of phenylacetylene dissolved in toluene to which had been added the same amount of alcohol as was used to solubilize water. Another sample of phenylacetylene was dissolved in water, and aliquots from it extracted as in the kinetic runs. The specific count in the extracted samples was 1.2 to 1.6 times that in the “water counting” conditions, but the exact factor varied with time, temperature of the freezer and precise condition of the counter, so that the relative count in water and extracted phenylacetylene could only be known to within some 25%, with a consequent similar error in the fractionation factor ϵ .

Results and Discussion

A. Hydroxide Ion Reaction.—Initial experiments were designed to obtain an accurate value of the rate coefficient for this reaction. Since at 25° the exchange has a convenient rate at a pH of about 8, we chose to use buffers of tri(hydroxymethyl)-methylamine ($pK_A = 8.08$) and its hydrogen chloride salt. Ionic strength was maintained at $\mu = 0.1$ using sodium chloride as necessary and the sum of the buffer components was kept constant at 0.02 M. The hydroxide ion concentration was varied by a factor of about nine by changing the buffer ratio. Table I gives the resulting data. The variation in $k/[OH^-]$, although not negligible, is apparently random. In particular there is no evidence for any contribution from catalysis by Tris itself. We conclude that under these conditions the exchange is accurately first order in hydroxide ion with a bimolecular rate coefficient of 2.7×10^2 .

Calculation of the hydroxide ion concentrations of Table I involves assumptions about activity coefficients. Our procedure was as follows. By treating the solution as if it were simply 0.1 M sodium chloride, we can obtain a value for K_w^c the self-dissociation constant for water.

$$[H^+][OH^-] = K_w^c = \frac{1 \times 10^{-14}}{\frac{\gamma_{H^+}\gamma_{OH^-}}{\alpha_{H_2O}}}$$

where the value of the activity coefficient ratio on the right is obtained from standard tables.⁷ For Tris and similar neutral bases we can write

$$K_A = \frac{[B][H^+]}{[BH^+]} \frac{\gamma_B\gamma_{H^+}}{\gamma_{BH^+}}$$

For dilute solutions we can assume that the activity coefficient correction is negligible, *i.e.*, $\gamma_B \approx 1$ and

(7) H. S. Harned and B. B. Owen, “The Physical Chemistry of Electrolytic Solutions,” Reinhold Corporation, New York, N. Y., 1950, p. 578.

$\gamma_{\text{H}^+}/\gamma_{\text{BH}^+} \approx 1$. Hence to the accuracy of our approximations

$$[\text{OH}^-] = \frac{K_w^{\text{H}}[\text{B}]}{K_a[\text{BH}^+]}$$

The assumption that $\gamma_{\text{B}} = 1$ will certainly be invalid for high concentrations of base. Furthermore the assumption $\gamma_{\text{H}^+} = \gamma_{\text{BH}^+}$ will probably be rather poor for bases of high molecular weight, *e.g.*, Tris or lutidine.

An approximate but useful check on the adequacy of these approximations is to measure the *pH* of the solutions with a glass electrode. For the solutions of Table I the observed changes in *pH* were, within experimental error, the same as the calculated.

TABLE I
DEPENDENCE OF EXCHANGE RATE FOR TRIS BUFFERS ON
HYDROXIDE ION CONCENTRATION

No. runs	$10^6[\text{OH}^-]$	$10^2[\text{Tris}]$	Average, 10^4k , sec. ⁻¹	$\frac{k}{[\text{OH}^-]}$
3	5.87	1.50	14.75 ± 0.3	252
3	3.26	1.25	$8.10 \pm .2$	248
3	1.96	1.00	$5.42 \pm .2$	278
2	1.17	0.75	$3.34 \pm .1$	286
2	0.65	0.50	$1.75 \pm .05$	270

Av. 267 ± 15

We have also investigated the catalytic activity of the base OD^- in the solvent D_2O , one reason being that data on relative rates can offer some corroboration of the postulated exchange mechanism. For this study comparison experiments were designed so that the only difference was in the solvent. A concentrated stock solution was prepared of a 5/1 $\text{Na}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ buffer. When diluted 1 to 50 by either water or D_2O , this led to solutions with ionic strength of 0.032 and with $[\text{HPO}_4^{2-}] = 0.01 M$ and $[\text{H}_2\text{PO}_4^-] = 0.002 M$. For the solution in water (and utilizing the Limiting Law) this leads to a hydroxide ion concentration of $6.7 \times 10^{-7} M$. However, the datum of particular interest for these studies is the ratio of the base concentration in the two solvents. This can be obtained in a straightforward way using the well established values for relative ionization of water and of dihydrogenphosphate ion.^{8,9} For the two pure solvents

$$\frac{[\text{OH}^-]}{[\text{OD}^-]} = \frac{K_w^{\text{H}} K_{\text{D}_2\text{PO}_4^-}^{\text{D}}}{K_w^{\text{D}} K_{\text{H}_2\text{PO}_4^-}^{\text{H}}} = \frac{6.5}{3.6} = 1.80$$

The observed data, as well as extrapolated values for the pure solvents, are listed in Table II. Using the extrapolation data, the ratio for the second order reaction of the hydroxide ions is given by

$$\frac{k_{\text{OD}^-}}{k_{\text{OH}^-}} = \frac{k_{\text{extrap}}^{\text{D}}[\text{OH}^-]}{k_{\text{OH}^-}^{\text{H}}} = \frac{1.40 \times 1.80}{1.88} = 1.34$$

This result is very close to the values given for relative rates of attack of other carbon-hydrogen bonds by these bases. Thus Pocker gives $k_{\text{OD}^-}/k_{\text{OH}^-} = 1.47$ for attack of the C-H bond in acetone¹⁰ and earlier studies at 5° give ratios of 1.36

(8) R. W. Kingerley and V. K. LaMer, *J. Am. Chem. Soc.*, **63**, 3256 (1941).

(9) C. K. Rule and V. K. LaMer, *ibid.*, **60**, 1974 (1938).

(10) Y. Pocker, *Chem. and Ind. (London)*, 1383 (1959).

and 1.39 for the similar reaction with nitroisopropane and nitroethane, respectively.¹¹ Even though there does not seem to be any reasonable alternative to the one-step proton transfer mechanism I, it is gratifying that the rate in deuterium oxide is consistent with this. The implication of all of these results is that OD^- in D_2O is a slightly stronger base than is OH^- in H_2O .

TABLE II

No. runs	D_2O , %	10^4k , sec. ⁻¹	10^4k for pure solvents
2	0	1.88 ± 0.06	1.88
2	97.5	1.41 ± 0.01	1.40^a

^a Extrapolated by formula $k^{\text{D}}/k^{\text{H}} = (k^{\text{D}}/k^{\text{H}})^n$ where *n* is atom fraction of D in solvent. (See E. A. Halevi, F. A. Long and M. A. Paul, *J. Am. Chem. Soc.*, **83**, 305 (1961).)

B. Water Reaction.—One advantage of the high sensitivity made possible by tritium labelling is that it permits a search for the "uncatalyzed" exchange. Since preliminary experiments had demonstrated the absence of acid catalysis, these studies were made in solutions that were 0.01 *M* in hydrochloric acid and 0.09 *M* in sodium chloride. Tritium labelled water was employed as the solvent, the activity being such that after artificial equilibration and conventional extraction the standard aliquot of phenylacetylene yielded a count of 1300 cpm. Solutions of unlabelled phenylacetylene were then prepared in the tritium-labelled solvent and left for 1.2×10^6 seconds (14 days). After the usual extraction this phenylacetylene showed an average count of $C = 0 \pm 15$ c.p.m., *i.e.*, zero within experimental error. This permits us to set an upper limit to the water rate: For the initial reaction

$$k_{\text{H}_2\text{O}} = \frac{1}{t} \frac{\Delta c}{c} = \frac{0 \pm 15}{1300} = 0 \pm 10^{-8} \text{ sec.}^{-1}$$

The first order rate coefficient for the water reaction is thus less than $10^{-8} \text{ sec.}^{-1}$. For the bimolecular reaction between the substrate and H_2O as a base, $k_{\text{bi}} < 2 \times 10^{-10} \text{ l. mole}^{-1} \text{ sec.}^{-1}$.

Comparison of this result with the rate coefficient for hydroxide ion permits a preliminary comment on the feasibility of detecting general catalysis. We note that $\log(k_{\text{bi}}^{\text{OH}^-}/k_{\text{bi}}^{\text{H}_2\text{O}}) > 12$ and that $\log(K_{\text{A}}^{\text{H}_2\text{O}^+}/K_{\text{A}}^{\text{H}_2\text{O}}) \approx 16$. It follows that, unless catalysis by hydroxide ion or water is anomalous, any general base catalysis will be characterized by a Brønsted β coefficient of at least 0.75. The implication is that catalysis by hydroxide ion will tend to dominate contributions from other bases. The results of the next sections are in accord with this.

C. Studies of General Base Catalysis. Tris Buffers.—The $[\text{B}]/[\text{BH}^+]$ ratio for these studies was maintained at 1/1 and the ionic strength was maintained at 0.1 using added sodium chloride when necessary. The nominal $[\text{OH}^-]$, calculated as outlined earlier, was $1.96 \times 10^{-6} M$. However, when both B and BH^+ concentrations approach 0.1 *M* one might expect the various activity coefficient assumptions to break down with a consequent drift in $[\text{OH}^-]$. As an additional difficulty the reproducibility of the

(11) S. A. Maron and V. K. LaMer, *J. Am. Chem. Soc.*, **60**, 2588 (1938).

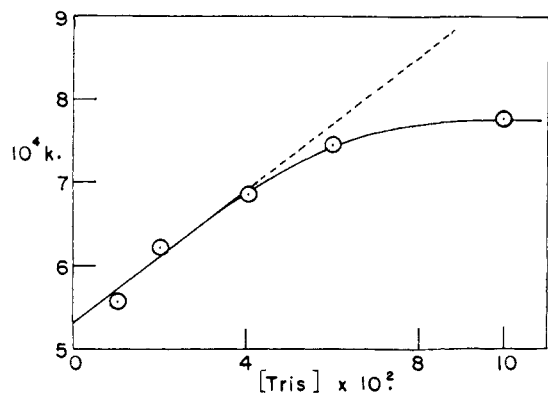


Fig. 2.—First order rate coefficients for studies with tris-(hydroxymethyl)-amine buffers at $\mu = 0.1$ and 1/1 buffer ratio.

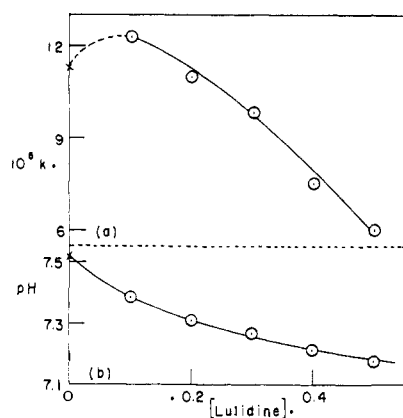


Fig. 3.—Rate coefficients and measured pH values for 2,6-lutidine buffers with $\mu = 0.1$ and $[\text{B}]/[\text{BH}^+] = 5/1$.

runs was poor for this buffer, standard deviations being in the order of $\pm 5\%$. Fig. 2 gives a plot of the average first order rate coefficients for these studies. The trend of the data is clearly non-linear. The curve drawn in the figure leads to $k_0^{\text{extrap}} = 5.30 \times 10^{-4}$, which with the above figure for $[\text{OH}^-]$ gives the previously calculated value of $k_2^{\text{OH}^-} = 2.7 \times 10^2 \text{ l. mole}^{-1} \text{ sec.}^{-1}$. The initial slope of the figure gives $k_2^{\text{Tris}} = 4 \times 10^{-3} \text{ l. mole}^{-1} \text{ sec.}^{-1}$ implying that the neutral base is a moderately good catalyst for the exchange. However, when one notes that the observed effect is not large, that the curve is nonlinear and that differential salt and solvent effects probably enter at the higher concentrations of buffer, one is forced to conclude that this evidence for general catalysis is less than compelling.

2,6-Lutidine Buffers.—With this weaker base ($\text{p}K_A = 6.72$) one can maintain ionic strength at the value $\mu = 0.1$ and yet increase considerably the concentration of the base species. The chosen buffer ratio was $[\text{B}]/[\text{BH}^+] = 5$ with base concentrations ranging from $[\text{B}] = 0.1$ to 0.5 M . The ionic strength was made up to 0.1 with potassium chloride. Using for this salt the same assumptions as in Part A, one calculates the nominal hydroxide concentration to be $4.2 \times 10^{-7} \text{ M}$ (nominal $\text{pH} = 7.52$).

Figure 3 gives the observed data for this system. The spectacular feature is that over the range

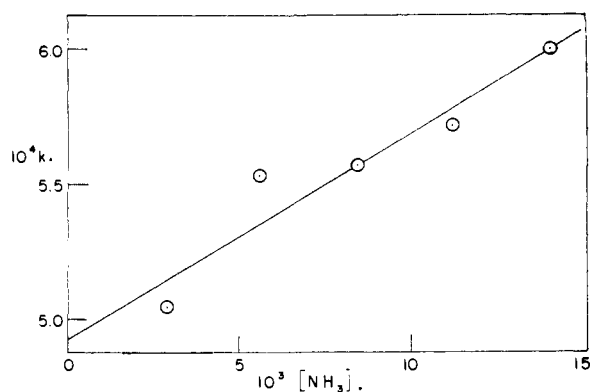


Fig. 4.—Ammonia buffers with $\mu = 0.3$ and $[\text{NH}_3]/[\text{NH}_4^+] = 0.047$.

studied, the first order rate coefficient at constant buffer ratio *decreases* with increasing concentration of base. If, however, one uses the previously established value of $k_2^{\text{OH}^-}$ to calculate the rate at zero buffer concentration, one can add the dotted portion of Fig. 3 and conclude that for low concentrations the rate probably increases with increasing buffer concentration reaching a maximum at about 0.1 M base and then decreasing. The most likely explanation of this behavior is that the assumption of $\gamma_B = 1$ fails. It seems probable that the self-interaction coefficient for 2,6-lutidine has a sizeable negative value leading to values of γ_B considerably less than unity for the higher concentrations of base.¹² This if true would lead to a decrease in the concentration of hydroxide ion as the lutidine concentration increases and would explain the observed drop in rate. One might reasonably expect a corresponding drop in pH and this is in fact observed as the lower part of Fig. 3 illustrates. We conclude that the combination of a large neutral base and its use at high concentrations make it impossible to reach any firm decision about general catalysis by lutidine.

Ammonia Buffers.—This system is *a priori* a favorable one for study. The base is comparatively strong ($K_A = 5.7 \times 10^{-10}$) so that only low concentrations of it need be employed. Although it is consequently necessary to use large concentrations of the acid, it is fortunately true that ammonium and potassium chlorides show such similar properties that the ionic strength principle is probably valid even at high salt concentrations. The particular choices were $\mu = 0.3$ maintained by use of these two salts and $[\text{NH}_3]/[\text{NH}_4^+] = 0.047$. For these conditions the hydroxide ion concentration calculates to $1.54 \times 10^{-6} \text{ M}$. In agreement with the assumption that these solutions were well-behaved, all of the buffer used in this study gave, within experimental error, the same measured pH .

Figure 4 gives the data for ammonia buffers. The plot is essentially linear and the slope leads to a bimolecular rate coefficient for ammonia of $k_2^{\text{NH}_3} = 7.5 \times 10^{-3} \text{ l. mole}^{-1} \text{ sec.}^{-1}$. Although reasonable, this value results from an uncomfortably small over-all change in rate, and consequently one's confidence in it cannot be high. As a different

(12) F. A. Long and W. F. McDevit, *Chem. Revs.*, **51**, 119 (1952), discuss the meaning and magnitude of self-interaction coefficients.

point, the extrapolated rate coefficient of Fig. 4 is $k_0 = 4.9 \times 10^{-4} \text{ sec.}^{-1}$. When combined with the calculated value of $[\text{OH}^-]$ it leads to $k_2^{\text{OH}^-} = 3.2 \times 10^2 \text{ l. mole}^{-1} \text{ sec.}^{-1}$, a significantly larger value than is observed at $\mu = 0.1$, but one which can perhaps be rationalized by consideration of the difference in ionic strength.¹³

To summarize, the data for all three of the weak bases studied do give evidence for the existence of general base catalysis even though in no one case is the evidence strong enough to be conclusive. One might hope to obtain further evidence by a study of other bases, but in fact considerations of solubilities and of base strength and type severely restrict the choices. Almost the only practical procedure for further study appears to be to turn to the relatively weak carboxylate ion bases and then to devise procedures for measuring the consequent very slow reactions.

D. Reverse Rate and Fractionation Factor.—

The previously discussed development of Bunton, Craig and Halevi⁵ requires for a tracer level exchange that the rate of the forward and reverse reactions should be the same, leading in both cases to the rate coefficient k_2 . This has now been investigated for the phenylacetylene exchange by experiments with two different catalyst solutions. The data are shown in Table III and Fig. 1 illustrates one pair of forward and reverse runs. For each of the catalyst solutions, the forward and reverse rates are the same within experimental error, in agreement with prediction.

TABLE III

No. runs	Base	Labeled material	$10^4 k$, sec. ⁻¹
5	Tris	C ₆ H ₅ C ₂ T	5.61 ± 0.35
3	Tris	HTO	5.76 ± 0.15
1	2,6-Lutidine	C ₆ H ₅ C ₂ T	1.23
2	2,6-Lutidine	HTO	1.26 ± 0.06

A related consideration is the fractionation factor ϵ , which at the tracer level is given by: $\epsilon = \alpha_\infty/\beta_\infty$. The conventional procedure for its determination requires allowing exchange to proceed to equilibrium and then measuring the isotopic abundance in both species. It is implicit in the earlier equation that ϵ can also be measured kinetically, a particularly useful procedure when the exchange is very slow or when side reactions do not allow precise equilibrium measurements.¹⁴ For the initial stages of the reverse reaction, when the label is in water at tracer level and the initial tritium abundance in phenylacetylene (α_0) is zero,

(13) The following experiment gives information on specific salt effects: Two solutions were made up to be identical with respect to the buffer in that $[\text{NH}_3]/[\text{NH}_4^+] = 0.47$ and $[\text{NH}_4^+] = 0.06 \text{ M}$ and also identical in total salt concentration 0.3 M , but with 0.24 M KCl as the added salt in one case, solution 1, and 0.24 M (CH₃)₄NCl for solution 2. There were slight but measurable differences in both rate and $p\text{H}$ for the two solutions. Specifically $k_{(2)}/k_{(1)} = 1.08$ and $\Delta p\text{H} = 0.04$ leading to $[\text{OH}^-]_{(2)}/[\text{OH}^-]_{(1)} \approx 1.1$. Although some such specificity is reasonably to be expected, it is noteworthy that the magnitude of the effect is not large enough to explain the observed behavior for Tris and particularly for lutidine buffers. This is consistent with the earlier conclusion that in these cases the effects are due to the high concentrations of the un-ionized bases themselves.

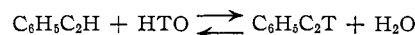
(14) Such a kinetic evaluation of ϵ has been carried out by J. Gutmann (*Internat. J. Appl. Radiation Isotopes*, **7**, 186 (1960)) using equations analogous to those of Bunton, Craig and Halevi, which he developed for exchange reactions on catalytic surfaces.

rearrangement of equation 2 leads to

$$\epsilon = \frac{1}{k_2\beta_0} \left(\frac{d\alpha}{dt} \right)_0 \quad (5)$$

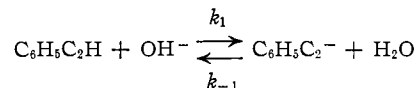
in which β_0 is the measured tritium abundance in the water and $(d\alpha/dt)_0$ is the initial rate of tritium build-up in the acetylene.

In the present case both the direct and kinetic methods were quite imprecise, since they both depended on tritium counting of C₆H₅C₂H and H₂O either under identical conditions, which is difficult, or with the use of a calibration procedure. The latter course was adopted in the present work, and principally due to the uncertainty in the calibration factor, ϵ could only be obtained to within about 25%. Within this precision, the kinetic and direct procedures led to the same value of the fractionation factor, which at 25° was $\epsilon = 0.46 \pm 0.06$. The equilibrium constant of the exchange reaction



is $\epsilon/2$ and hence is 0.23 ± 0.03 .¹⁵

E. Rate of Proton Transfer to the Anion.—The degree of dissociation of phenylacetylene as an acid was studied some time ago by Conant and Wheland¹⁶ and by McEwen¹⁷ who assigned it a pK_A value of 22, based on a pK_A of 18 for ethanol. Since ethanol is now known to have a pK_A of very close to 16,¹⁸ we shall assume $pK_A = 20$ for phenylacetylene. This value can be combined with the kinetic data of the previous sections to give information on the kinetics of neutralization of the phenylacetylene anion. Consider the equilibrium



Although k_1 for this reaction (rupture of the CH bond in protophenylacetylene) has not been measured, it can be approximated rather closely since we know the analogous rate coefficient for C₆H₅C₂T and can assume that rupture of a C—H

(15) One can obtain a more precise evaluation of the equivalence of the two methods of measuring ϵ by a somewhat different procedure. Suppose we insist that the two ϵ values are identical, i.e., that $\epsilon_{\text{kin}} = \epsilon_{\text{eq}}$. This can be expressed as

$$\frac{\alpha_\infty}{\beta_\infty} = \frac{1}{k_2\beta_0} \left(\frac{d\alpha}{dt} \right)_0$$

Since water is in very great excess, $\beta_\infty \approx \beta_0$, and

$$\frac{1}{\alpha_\infty} \left(\frac{d\alpha}{dt} \right)_0 = k_2$$

Noting that $(C_\infty - C_0)$, the equilibrium net count per minute per aliquot, is proportional to α_∞ , we have as our test of equivalence

$$k_2 = \frac{1}{(C_\infty - C_0)} \left(\frac{dC}{dt} \right)_0$$

To illustrate a specific test, consider the reverse run of Fig. 1. The logarithmic plot leads to $k_2 = 1.21 \times 10^{-4} \text{ sec.}^{-1}$. A direct plot of C against the time yields both an intercept ($C_0 = 40 \text{ c.p.m. aliquot}$) and an initial slope $\left(\left(\frac{dC}{dt} \right)_0 = 0.05 \text{ c.p.m./aliquot/second} \right)$. Since for this run C_∞ was $425 \text{ c.p.m./aliquot}$, we obtain

$$\frac{1}{(C_\infty - C_0)} \left(\frac{dC}{dt} \right)_0 = 1.3 \times 10^{-4} \text{ sec.}^{-1}$$

The agreement of this value with that of k_2 confirms the equivalence of the two methods.

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

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

(18) P. Ballinger and F. A. Long, *ibid.*, **82**, 795 (1960).

bond will be about 10-fold faster than that of a C-T bond. Hence $k_1 \simeq 3 \times 10^8$ l. mol⁻¹ sec.⁻¹. For the above reaction

$$\frac{k_1}{k_{-1}} = K_{\text{eq}} = \frac{K_a[\text{H}_2\text{O}]}{K_w}$$

From this we calculate that for the reaction of the anion and water $k_1 \simeq 10^8$ l. mole⁻¹ sec.⁻¹.

For the analogous reaction of phenylacetylene with water, it was concluded that $k_{\text{bi}} < 2 \times 10^{-10}$ l. mole⁻¹ sec.⁻¹. Combining this with the pK value implies only that k for reaction of $\text{C}_6\text{H}_5\text{C}_2^-$ and H_3O^+ is less than 10^{12} . Actually by considering the expected rate for diffusion controlled neutraliza-

tion reactions,¹⁹ we can set a limit of between 10^{10} and 10^{11} (the value for a diffusion controlled process) for this rate coefficient. Since one will surely except neutralization by H_3O^+ to be faster than by H_2O , this upper limit is probably close to the actual value.²⁰ It thus appears that the anion of an acetylene derivative belongs to the group of "fast" proton acceptors.¹⁹

(19) R. P. Bell, *Quart. Revs. (London)*, **13**, 169 (1959).

(20) For the forward and reverse of a general catalyzed proton transfer reaction, the sums of the Brønsted coefficients should equal unity. Since we have concluded that β for reaction of phenylacetylene with bases was above 0.8, it follows that α should be less than 0.2, perhaps 0.15. Some such figure as this is consistent with the above rate coefficients for reaction of the anion.

[CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

The Crystal Structure of Ethylenediamine Tribromoplatinum ($\text{C}_2\text{N}_2\text{H}_8$)PtBr₃¹

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Pt(en)Br₃ is a complex between Pt(en)Br₂ and Pt(en)Br₄. The orthorhombic crystals, $a = 5.60$, $b = 14.77$, $c = 10.12$ Å. contain Pt(IV)enBr₂ and Pt(II)enBr₂ planar (or nearly planar) groups lying parallel to (100) and connected with essentially linear, ordered, Pt(II) ··· Br-Pt(IV)-Br ··· Pt(II) ··· chains running along a . Between chains Pt(II) and Pt(IV) positions can be exchanged at random. The distance Pt(IV)-Br along the chains is 2.48 Å., and the average Pt(II)-Br, Pt(IV)-Br distance within the planar groups is 2.51 Å., not significantly different. Light with its electric vector along the chains is very strongly absorbed. Presumably this is a charge transfer absorption.

Introduction

The compound with the empirical formula, Pt(en)Br₃ (en = $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$), is of interest because of its relation to the problem of the possibility of Pt(III). The structure reported here confirms the chemical evidence which has been given to show that Pt(II) and Pt(IV) in equal amounts lead to an average valence.² The compound is of further interest because of its strong pleochroism, the crystallographic distinction between Pt(II) and Pt(IV) and a type of disorder found in the crystal. It is far from an ideal crystal for the study of metal-ethylenediamine rings, and in our work only heavy atom positions and their relation to the points of interest above have been given attention. The heavy atoms, except for a point with respect to the disorder, are found without difficulty, and details of the structure determination are not discussed here.

Our attention was drawn to this problem by Prof. R. E. McCarley of this Laboratory, who made the compound and supplied us with crystals.

The crystals form very thin, orthorhombic blades of an iridescent green. In polarized light they are light yellow when viewed with the electric vector normal to the blade axis, but black and nearly completely absorbing, even in very thin crystals, when the electric vector is along the blade axis.

The lattice constants are $a = 5.60$ (blade axis), $b = 14.77$, $c = 10.12$ Å.; $\rho_{\text{obsd.}} = 4.03$ g./cc. *vs.*

(1) Contribution No. 884. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Based on a thesis submitted by T. D. R. to Iowa State University in partial fulfillment of the requirements for the degree of Master of Science.

(2) G. W. Watt and R. E. McCarley, *J. Am. Chem. Soc.*, **79**, 4585 (1957).

$\rho_{\text{x-ray}} = 4.027$ for four Pt(en)Br₃ per cell. (Lattice constants b and c were determined from back reflection Weissenberg diagrams, a from precession diagrams using b or c for internal calibration.)

Since reflections $\{hkl\}$ are observed only for $h + k = 2n$, and $\{h0l\}$ only for $h = 2n$, $l = 2n$, the possible space groups are Cmc₂, Cmc₂₁ and C2cm. Though platinum and bromine positions were found in Cmc₂, the true space group must be C2cm if the Pt(en) rings are non-planar, as expected.³

Oscillation photographs taken with a as the rotation axis showed pronounced streaks between layer lines. The reason for this streaking is made clear by the structure determination (*vide infra*). Intensities $\{0kl\}$, $\{hk0\}$ and $\{h0l\}$ were determined visually from timed and/or multiple film Weissenberg and precession diagrams. Anomalous dispersion,⁴ Lorentz and polarization factors were taken into account, but since no absorption corrections were made, this is a factor limiting the accuracy of the structure reported below.

Patterson functions gave platinum and rough bromine positions very simply. It was at first supposed that the twelve bromine atoms would be found in an eight-fold set and in a four-fold set, but it became evident that four of the bromine atoms must be distributed at random in an eight-fold set.

Parameters were refined using reflections from all three zones and a least squares program supplied by Templeton and Senko. The discrepancy factors, $R = \frac{\sum |F_0| - |F_c|}{\sum |F_0|}$ were 0.079, 0.124

(3) See, for example, A. Hakahara, Y. Saito and H. Kuroya, *Bull. Chem. Soc. (Japan)*, **25**, 331 (1952).

(4) D. Templeton and C. H. Dauben, *Acta Cryst.*, **8**, 841 (1955).