Therefore, convection cannot cause the observed values of D in the H_2O–D_2O experiments to stray appreciably outside the range from D_i to D_o. Thus we would have observed easily the enormous decrease of D reported by Adamson and Irani, and we must conclude that their measurements are erroneous.

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THE PREPARATION OF A CRYSTALLINE gem-DITHIOL UNDER MILD CONDITIONS

Sir:

We wish to report the synthesis in 80% yield of the first crystalline *gem*-dithiol, 2,2-dimercapto-1,3-diphenylpropane, m.p. 81.5–83°, by the combined action of hydrogen sulfide and hydrogen chloride upon dibenzyl ketone at atmospheric pressure. Since these conditions heretofore have been used for the preparation of thioketones and thioaldehydes (or their polymers) in variable yield,[1] we believe that previous investigators have failed to recognize that *gem*-dithiols are among the reaction products because the reaction mixtures have been worked up by the use of procedures which would have destroyed *gem*-dithiols. It seems likely that the formation of *gem*-dithiols from carbonyl compounds is of far greater generality than has been recognized up to the present time, and that their presence can explain some puzzling reaction products which have been observed. We are exploring the scope of the reaction, as well as the chemistry of *gem*-dithiols, broadly. The first previous synthesis[2] of *gem*-dithiols utilized pressures in the range of 35–8500 atmospheres without added catalysts, and yields were commonly 15 to 35%.

A solution of dibenzyl ketone (19.4 g., 0.0924 mole) in 50 ml. of ethanol was cooled in an ice-bath. Dry hydrogen chloride and dry hydrogen sulfide were simultaneously bubbled through the solution for a period of six hours. The reaction mixture was allowed to stand overnight in a refrigerator. The precipitate was filtered, washed with cold ethanol, and dried in air to yield 19.6 g. (80%) of colorless, granular crystals, m.p. 75–80°. Two recrystallizations from ethanol (at temperatures not exceeding 50°) yielded 15 g. of colorless needles, m.p. 81.5–83°. Infrared absorption at 2570 cm.$^{-1}$ showed the presence of the sulfhydryl group; carbonyl absorption was absent. Sodium nitroprusside gave a positive sulfhydryl test. Lead acetate produced a yellow precipitate which slowly turned black on standing, a behavior typical of *gem*-dithiols.[2] *Anal.* Calcd. for $C_{15}H_{16}S_2$: C, 69.18; H, 6.19; S, 24.63. Found: C, 69.41; H, 6.31; S, 24.63.

The *gem*-dithiol yielded with 2,4-dinitrophenylhydrazine reagent the same orange crystalline 2,4-dinitrophenylhydrazone as dibenzyl ketone, m.p. 98.5–99.5° after recrystallization from ethanol. Identification was made by comparison of melting points (no depression on admixture) and infrared absorption spectra.

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[1] (a) A. Schönberg, p. 705 ff., in "Methoden der organischen Chemie," (Houben-Weyl), 4th ed. (ed. E. Müller), G. Thieme, Stuttgart, Vol. 9, 1955; (b) E. Campaigne, *Chem. Rev.*, **39**, 1 (1946).

[2] T. L. Cairns, G. L. Evans, A. W. Larcher and B. C. McKusick, THIS JOURNAL, **74**, 3982 (1952).

EXCHANGE RATES OF ACETYLENIC HYDROGENS IN AQUEOUS SOLUTIONS[1]

Sir:

Available studies on the exchange of acetylenic hydrogens with those of aqueous solutions do not establish definitely the details of the exchange process but do imply that the rate is only moderate, even when the aqueous phase contains one molar hydroxide ion.[2,3] In view of the acidic character of acetylenes,[4,5] this is surprisingly slow. We have consequently reinvestigated this exchange for phenylacetylene and for acetylene itself. For the first of these, $C_6H_5C_2D$ was prepared and aliquots were shaken with aqueous buffer solutions at 25°. Analysis was made with an infrared spectrometer on solutions of the phenylacetylene in carbon tetrachloride. In the second case, acetylene was shaken at 25° with buffers made up with water which contained 60 atom per cent. deuterium. Analysis of the C_2HD formed was made by gas phase infrared. In both cases the aqueous hydrogens were in large excess and only initial rates were measured so that reverse processes can be neglected. At pH values below ten the rate of exchange easily could be made independent of the degree of shaking, indicating that the slow step occurred in the aqueous phase. We therefore have used the observed half-times for exchange and the measured mole ratios and solubilities to calculate the listed values of the first order rate coefficients for the solution reaction. The relevant equation is $k_{\text{soln}} = 0.69A/V_BSt_{1/2}$, where A is total moles and S is aqueous solubility of the acetylene compound, V_B is volume of aqueous phase and $t_{1/2}$ is the observed half-time for the two-phase exchange.

Solution	pH	$10^6k_{\text{soln.}}$, sec.$^{-1}$
	Acetylene	
0.02 M total phosphate	8.60	2600
0.02 M total phosphate	9.04	6000
	Phenylacetylene	
0.01 M HCl	2	no exchn.
0.04 M total acetate	5.03	2
0.02 M total phosphate	7.03	71
0.02 M total phosphate	7.91	510
0.02 M total phosphate	8.60	1300
0.05 M total phosphate	8.60	1500
0.014 M total borate	9.0	4600
0.012 M total borate	9.5	12000

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[1] Work supported by a grant from the Atomic Energy Commission.

[2] L. H. Reyerson and S. Yuster, THIS JOURNAL, **56**, 1426 (1934); **57**, 779 (1935); see also L. H. Reyerson and B. Gillespie, *ibid.*, **57**, 2250 (1935); **58**, 282 (1936); and **59**, 901 (1937).

[3] R. P. Bell, *ibid.*, **57**, 778 (1935).

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

[5] W. K. McEwen, *ibid.*, **58**, 1124 (1936).

The data support the assumption of a slow, aqueous phase rate step and show that both exchange reactions are base catalyzed. The intrinsic rates for the two compounds are large and are quite similar. The data for phenylacetylene indicate that neither water nor hydrogen ion is an effective catalyst. They also suggest that for all conditions the predominant base catalyst is hydroxide ion. This is of interest since the expected mechanism for this exchange predicts general base catalysis. The second order rate coefficient for reaction of phenylacetylene-d_1 and hydroxide ion is 460 l. mole^{-1} sec.$^{-1}$, which is close to the value reported in the accompanying communication by Kreevoy and coworkers for the analogous exchange of the hydrogen compound in aqueous pyridine.[6] Further work is in progress.

(6) H. B. Charman, M. Kreevoy, G. V. D. Tiers and G. Filipovich, *J. Am. Chem. Soc.*, **81**, 3149 (1959).

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RATE OF BASE CATALYZED HYDROGEN EXCHANGE BETWEEN PHENYLACETYLENE AND WATER

Sir:

The rate of exchange of the acidic hydrogen of phenylacetylene with water in 9% by volume aqueous pyridine is first-order with respect to both acetylene and hydroxide ion. The rate-determining step is presumably the abstraction of a proton from phenylacetylene by the base. Rates were measured from the broadening of the acetylenic hydrogen n.m.r. peak caused by the exchange. The second-order rate constant, $k_2 = 3.5 \pm 0.5 \times 10^3$ m.$^{-1}$ sec.$^{-1}$, is in satisfactory agreement with that obtained in water by deuterium exchange[1] ($k_2 =$ 460 m.$^{-1}$ sec.$^{-1}$) when the isotope effect and difference in solvent are considered.

Our results and those of Long and Ballinger[1] indicate that k_2 in water is $\sim 10^3$ m.$^{-1}$ sec.$^{-1}$ from which ΔF^* is $\sim$13 kcal. mole^{-1}. McEwen[2] has estimated pK_a for phenylacetylene in water as 21. Combining this with the pK for dissociation of water, ΔF^0 for the reaction of phenylacetylene with hydroxide ion is $\sim$7 kcal. mole^{-1}. The difference between these numbers is the free energy of activation for the reaction of the phenylacetylide ion with water. Since ΔS^0 for liquid water at 25° is 17 cal. mole^{-1} deg.$^{-1}$, the free energy increase accompanying the total immobilization of a water molecule would be $\sim$5 kcal. mole^{-1}.

Aqueous pyridine was chosen as the solvent so as to separate the acetylenic hydrogen peak from the solvent spectrum. Peak height is approximately proportional to the transverse relaxation time, T_2.[3] The exchange process provides an additional mode of relaxation so that the acetylenic hydrogen peak height is proportional to the effective relaxation time τ_2, where $1/\tau_2 = 1/T_2 + k_1$, k_1 being the first order rate constant for the exchange. T_2 was not constant, and it even varied during a single sweep. To apply a correction methanol ($\sim$2%) was included in the solvent, and the height of the methyl peak was measured and taken as proportional to T_2.

The second-order rate constants tabulated were obtained using 10^{-2}–10^{-4} *M* tetramethylammonium hydroxide at 24.5 ± 1°. The first of these was invariant (within its uncertainty) under a 10-fold variation in hydroxide ion concentration.

Water, % v.	$PhC\equiv CH$, % v.	$10^{-3}k_2$
9.1	2.8	3.5 ± 0.7
9.1	9.1	3.4 ± 0.4
15.1	9.4	1.2 ± 0.3[a]

[a] Dimethyl sulfoxide and mesitylene were used in place of methanol for some runs in this solvent.

In 10% aqueous pyridine there was a nearly linear relation between base concentration and conductivity, giving a limiting equivalent conductance of $\sim$30 ohms^{-1} cm.^{2}. The ratio of the viscosity of 10% aqueous pyridine to that of water is 1.7 at 25°. This suggests that the base exists principally as free ions in this solvent.

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(1) F. A. Long and P. Ballinger, THIS JOURNAL, **81**, 3148 (1959).

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

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

APPLICATION OF MASS SPECTROMETRY TO STRUCTURE PROBLEMS. II. STEREOCHEMISTRY OF EPIMERIC, CYCLIC ALCOHOLS

Sir:

During an investigation of the mass spectra of epimeric, cyclic alcohols, we have observed that the spectra of epimers, which are in general very similar as is to be expected, differ distinctly in the abundance of the molecular ion, M$^+$. This peak was found to be more intense in the spectrum of the less crowded epimer (equatorial hydroxyl) of secondary alcohols, whereas in tertiary alcohols the epimer with the axial hydroxyl and equatorial alkyl group exhibited the more intense M$^+$ peak (Table I).

We interpret this effect as a consequence of a different rate of decomposition into fragments of the molecular ion (M$^+$), formed on electron impact, which is slower in the case of the more stable ion M$^+$. (Since the fragments of the two isomers are the same, their formation need not be considered; the ionization step cannot give rise to the observed difference because the cross sections of epimeric alcohols are at least nearly the same.)

A secondary, cyclic alcohol with the hydroxyl group in the more crowded position will therefore yield a molecular ion which has a greater tendency to decompose (and show a less intense M$^+$ peak) than its less crowded epimer. Since a hydroxyl group requires less space than an alkyl group, the situation is reversed in the case of tertiary alcohols.

The spectra of the acetates of secondary alcohols show the same effect, enhanced due to the larger size of the acetoxy group compared with hydroxyl.

The main difference in the decomposition of M$^+$ appears to be in the path leading to the fragment M-18 (or M-60 for the acetates) whose abundance is in turn always greater for the more crowded epimer.