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).

DEPARTMENT OF CHEMISTRY
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RECEIVED APRIL 25, 1959

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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RECEIVED APRIL 23, 1959

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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.

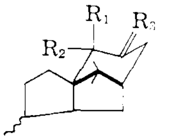
The spectra of the acetates of secondary alcohols show the same effect, enhanced due to the larger size of the acetoxy group compared with hydroxyl.

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.

TABLE I

Secondary alcohols	Abundance[a] of ion M	(M-18)
Borneol	0.17	1.47
Isoborneol	0.14	2.41
exo-cis-Bicyclo[3.3.0]octan-2-ol[b]	1.44	3.53
endo-cis-Bicyclo[3.3.0]octan-2-ol[b]	0.36	4.02
Epiandrosterone	4.58	0.53
Androsterone	3.53	0.66
cis-cis-2-Decalol[c]	0.08	8.22
cis-trans-2-Decalol[c]	0.02	10.62
Tertiary alcohols		
Patchouli alcohol (I)[d]	3.46	0.70
Epipatchouli alcohol (II)[d]	0.045	4.52
Oxo-patchouli alcohol (III)[d]	1.55	0.51
Oxo-epipatchouli alcohol (IV)[d]	0.2	0.15
Epimaaliol[e]	0.48	2.74
Maaliol[e]	0.09	3.03
Secondary acetates	M	(M-60)
Borneol acetate	0.31	5.08
Isoborneol acetate	0.04	5.94
Epiandrosterone acetate	1.07	4.56
Androsterone acetate	0.29	5.98

[a] % of total ion yield. Spectra taken with a CEC 21-103C mass spectrometer; inlet temp. 140°. [b] A. C. Cope, M. Brown and H. E. Petree, THIS JOURNAL, **80,** 2852 (1958). [c] W. G. Dauben and E. Hoerger, *ibid.*, **73,** 1504 (1951). [d] G. Büchi, R. E. Erickson and N. Wakabayashi, to be published. [e] G. Büchi, M. Schach v. Wittenau and D. M. White, *ibid.*, **81,** 1968 (1959).



I, $R_1 = OH$, $R_2 = CH_3$, $R_3 = H_2$
II, $R_2 = CH_3$, $R_2 = OH$, $R_3 = H_2$
III, $R_1 = OH$, $R_2 = CH_3$, $R_3 = O$
IV, $R_1 = CH_3$, $R_2 = OH$, $R_3 = O$

Thus, if the molecular models of epimeric alcohols show an appreciable[1] difference in their steric requirements, the mass spectra should allow the assignment of their stereochemistry.

We are indebted to Professors G. Büchi, A. C. Cope and W. G. Dauben for generous gifts of samples and to the National Science Foundation for financial support (Grant G 5051).

[1] For example, *exo*- and *endo*-norborneol gave inconclusive results.

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NIOBIUM TETRAIODIDE: ITS STRUCTURE AND NATURE OF BONDING[1]

Sir:

Since the preparation of NbI_4 by Corbett and Seabaugh[2] there has been some question as to whether the tetravalent oxidation state of niobium exists in the solid state. One normally would expect NbI_4 to possess one unpaired electron and hence be paramagnetic if the niobium were indeed tetravalent. Recently Rolsten[3] reported the presumably isomorphous TaI_4 to be diamagnetic. Rolsten speculated that the unpaired electron must be paired by the formation of a dimer, or else TaI_4 may exist in the solid state as $Ta^{+3}Ta^{+5}I_8$. We wish to report the preliminary results of the structural determination of NbI_4 by X-ray diffraction and strong evidence of metal–metal interaction which will readily explain its diamagnetism as well as that of TaI_4.

Single crystals of NbI_4 were generously furnished to us by Corbett and Seabaugh. Since the compound is extremely sensitive to water and oxygen the crystals were isolated in glass capillaries which were first evacuated and then hermetically sealed. Three dimensional X-ray data were taken with both Weissenberg and precession cameras utilizing MoKα radiation. The crystals are orthorhombic with space group $Cmc2_1$ and lattice constants a = 7.67 Å., b = 13.28 Å., and c = 13.93 Å. There are eight NbI_4 species per unit cell.

Patterson and Fourier projections of the three principal zones gave the essential features of the structure. A least squares refinement of the observed reflections resulted in values of $R = \Sigma|F_0| - |F_c|/\Sigma|F_0| < 0.14$ for each zone.

The structure consists of infinite chains parallel to the "a" axis formed by NbI_6 octahedra sharing two opposite edges. The niobium atoms are shifted from the centers of the octahedra of iodine atoms, which are 3.83 Å. apart, toward each other in pairs such that the distance between the paired niobium atoms is 3.2 Å. The only reasonable explanation for this shift involves a metal–metal interaction in which the unpaired electrons are coupled by exchange forming a weak metal–metal bond. It should be noted that NbI_4 was first reported to be paramagnetic; in view of our structural results a redetermination of the magnetic moment by Corbett and Seabaugh[4] revealed NbI_4 to be diamagnetic at room temperature. This compound represents the first known structure of its configuration which possesses metal–metal interactions.

A qualitative interpretation of the nature of bonding about each niobium atom can be given in terms of simple molecular orbital theory based on octahedral symmetry. The d_{z^2} and $d_{x^2-y^2}$ metal orbitals plus the one 5s and three 5p metal orbitals interact with the corresponding symmetry orbitals of the iodides to give bonding σ-type molecular orbitals. The unshared electron for each niobium can be placed in the d_{xy} orbital; the metal–metal bond for two paired niobiums is thus accomplished by the overlap of these two neighboring orbitals which are directed toward each other (*i.e.*, the x and y axes are along the shared iodide directions). The unoccupied d_{xz} and d_{yz} orbitals of each niobium no doubt are utilized in π-bonding with the filled π-type symmetry orbitals of the iodides.

Since the diamagnetism of TaI_4 can be explained easily by a similar structure, and especially since X-ray data on TaI_5[3] indicate its structure to be directly related to that of NbI_5[5] (*i.e.*, the lattice con-

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[1] Presented in part before the Division of Physical Chemistry, American Chemical Society Meeting, April 5–10, 1959.

[2] J. Corbett and P. Seabaugh, *J. Inorg. Nucl. Chem.*, **6**, 207 (1958).

[3] R. Rolsten, THIS JOURNAL, **80**, 2952 (1958).

[4] J. Corbett and P. Seabaugh, private communication.

[5] L. Dahl and N. Nelson, to be published.