Table I. Proton–Proton Coupling Constants (Hz)

Compound	J_{12}	J_{13}	J_{23}	J_{23}'	J_{22}'	J_{33}'	Source
C_5H_6	+1.36	−1.52	+5.06	+1.09	+1.98	+1.90	*a*
1	±1.17	±0.01	+4.66	+1.15	+2.02	+2.02	*b*
2	±1.22	±0.10	4.64	1.17	2.06	2.12	*b*
Indene	2.02	−1.98	5.58				*c*
$(h^5\text{-}C_5H_5)Fe(CO)_2(h^1\text{-}C_9H_7)$	~2.3	~0	5.5				*d*

[a] S. L. Manatt, personal communication. [b] This work. [c] D. D. Elleman and S. L. Manatt, *J. Chem. Phys.*, **36**, 2346 (1962). [d] Reference 3.

(2) To reconcile solution pmr data[8] and the crystal structure[9] of $(C_5H_5)_3MoNO$, it has been proposed[9] that in solution the conformers **3a** and the enantiomorphous forms of **3b** cease to be rapidly interconverted and, for any given molecule, one enantiomorph of **3b** increasingly predominates below about −60°. This explains why two C_5H_5 rings which are equivalently bonded to the Mo atom become nonequivalent in the pmr spectrum, while the olefinic multiplet of the $(h^1\text{-}C_5H_5)$ group *simultaneously* breaks up into a more complex pattern.[8] The details of this breakup provide support for 1,2-shifts by confirming the assignment of the signal at lower field to H(2), H(2′). Thus, it is the low-field side which again collapses *below* −50°, ultimately giving rise to two signals each of intensity appropriate to one proton. This can be attributed to the molecule settling into one of the **3b** configurations (both are found in the crystal[9]), in which the H(2), H(2′) protons sense their different environments strongly due to their proximity to the $(C_5H_5)_2MoNO$ moiety, while the H(3), H(3′) protons are much further away and sense the differences much less. Assignment of the low-field signal to H(2), H(2′) is thus required.

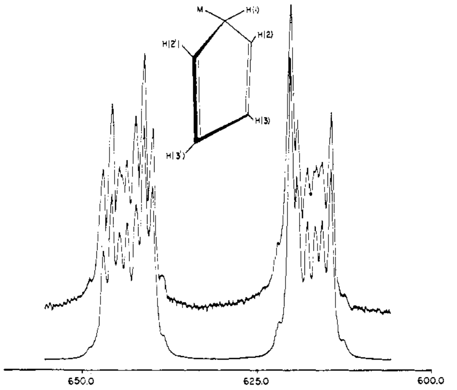

Figure 2. Upper trace: part of the limiting low temperature spectrum of $(h^5\text{-}C_5H_5)Ru(CO)_2(h^1\text{-}C_5H_5)$ recorded at −82° in 3:1 (v/v) CS_2–$C_6D_5CD_3$ at 100 MHz. Abscissa: Hz *vs.* TMS. Lower curve: computer simulated spectrum using *J* values given in Table I.

Relevant to considerations of rotational isomers of types **3a** and **3b** are some observations on **1** and **2**. Under high resolution in cyclohexane, the infrared spectra of **1** and **2** show four CO stretching bands. For **1**: 2022, 2016, 1973, 1966 cm^{-1}; for **2**: 2030, 2023, 1976, 1969 cm^{-1}. The components of each doublet have an intensity ratio of 2 ± 1 which changes by only 5–10% from −65 to +35°. We attribute these observations to approximately equal population of conformers **1a** and **1b**, **2a** and **2b**, with ΔH for **a**–**b** interconversions <0.5 kcal. In crystalline **1**,[2] **1a** is found.

2870 (1963), correlates J_{12} with ϕ, obtaining $J_{12} \approx$ 2–3 Hz for $\phi \approx 60°$ and $J_{12} \rightarrow 0$ as $\phi \rightarrow 90°$. The actual ϕ in **3** is about 56°, while that in cyclopentadiene (Professor V. Laurie, Princeton University, private communication) is about 55°.

(8) F. A. Cotton and P. Legzdins, *J. Amer. Chem. Soc.*, **90**, 6232 (1968), and further studies by the present authors.

(9) J. L. Calderon, F. A. Cotton, and P. Legzdins, *ibid.*, **91**, 2528 (1969).

(10) National Science Foundation Predoctoral Fellow, 1966–1970.

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Third-Order Rates of Conversion of Phenylacetylene, a Weak Carbon Acid, by Sodium Hypochlorite to Phenylchloroacetylene and by Sodium Hypobromite to Phenylbromoacetylene

Sir:

It is commonly accepted that the halogenation of weak carbon acids, *e.g.*, ketones, nitriles, nitroalkanes, etc., in basic solution is first order in CH, first order in base, and zero order in halogen (eq 2).[1] We now report

$$\begin{gathered} CH + OH^- \xrightarrow{\text{slow}} C^- + H_2O \\ C^- + X_2 \xrightarrow{\text{fast}} CX + X^- \end{gathered} \tag{1}$$

$$\text{rate} = k[CH][OH^-][X_2]^0 \tag{2}$$

a third-order rate law (eq 3) for halogenation ($X_2 = Cl_2$

$$\text{rate} = k[C_6H_5C{\equiv}CH][OH^-][XO^-] \tag{3}$$

or Br_2) of the hydrocarbon phenylacetylene, according to the stoichiometry of eq 4.

$$C_6H_5C{\equiv}CH + OH^- + X_2 \longrightarrow C_6H_5C{\equiv}CX + H_2O + X^- \tag{4}$$

Some of the kinetic data obtained for reaction 4 are given in Table I. In the range pH >11 and $[OH^-]_0 > 2[X_2]_0$, the equilibrium constants for chlorine and bromine in eq 5 are $K \simeq 10^{15}$ and 10^8, respectively,[2] so that

$$2OH^- + X_2 \rightleftharpoons XO^- + X^- + H_2O \tag{5}$$

essentially all of the halogen is in the form of hypohalite ions. (In the range $[X_2]_0 \simeq 2[OH]_0$ in which X_2 or HOX are present, competing additions to phenylacetylene complicate this system.) The formation of phenylhaloacetylene was followed spectrophotometrically

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(1) (a) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Chapters IX, X; (b) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., Chapter 9.

(2) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1966, p 570.

Table I. Rate Data for the Reaction of Phenylacetylene with Chlorine or Bromine in Excess Sodium Hydroxide

Solvent	Temp, °C	$[C_6H_5C{\equiv}CH] \times 10^4$, M	[NaOH],[a] M	$[OCl^-]$ or $[OBr^-]$,[a] M	No. of runs	k, M^{-2} $sec^{-1} \times 10^3$
H_2O	46.1	1.3–1.7	0.07–0.7	0.02–0.09	8	2.13
H_2O	25.3	1.5–1.7	0.07–0.9	0.04–0.09	7	0.462
D_2O	46.1	1.5–2.2	0.3–0.6	0.03–0.06	4	2.12
H_2O	25.0	1.27	1.82	0.049	1	1.12
H_2O	46.1	1.94	0.242	0.0946	1	3.31[b]
H_2O	46.1	1.68	0.242	0.0946	1	4.40[c]
H_2O	27.5	0.6–0.9	0.02–0.14	0.001–0.01[a]	15	7000[a]

[a] These are not initial concentrations, but those that refer to the solution determined by eq 5 and before process 4 has started. Only the last entry refers to hypobromite runs. [b] In 0.625 M NaCl. [c] In 0.625 M Na_2SO_4.

and was cleanly third order (eq 3) over the concentration range of sodium hydroxide 0–0.9 M. At higher concentrations of sodium hydroxide or with added salts, the rate constants for process 4 are markedly increased. The rate constant for chlorination in deuterium oxide is the same as that in water. The ratio of third-order rate constants $k(Br_2)/k(Cl_2) \simeq 10^4$ at 27.5°.

We propose that the mechanism of these halogenations involves the rapid proton ($k_6 \simeq 3 \times 10^3$ M^{-1} sec^{-1} at 25°)[3] exchange of eq 6 followed by rate-determining attack of hypohalite on phenylacetylide. The absence of a deuterium isotope effect in the chlorination (k_6k_7/k_{-6}) is curious, but not inconsistent with eq 6.

$$C_6H_5C{\equiv}CH + OH^- \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} C_6H_5C{\equiv}C^- + H_2O$$

$$C_6H_5C{\equiv}C^- + OX^- \xrightarrow[k_7]{\text{slow}} (C_6H_5CCXO)^{2-} \xrightarrow{\text{fast}} C_6H_5C{\equiv}CX \qquad (6)$$

The effect of salts (and sodium hydroxide) in increasing the rate has precedent in other reactions between negative ions[4,5] and is in contrast to their effect on rate law (2).[6] Although Rappe has dismissed the doubly charged transition state as implausible,[7] it appears that we are probably dealing with such a species.

The halogenation reaction plays a key role in the theory and practice of basic catalysis of carbon acids such as ketones, nitroalkanes, cyanoalkanes, etc. Occasional variations from the relation of eq 2 to process 1 have usually been associated with extremely low halogen or carbanion concentrations.[1a,8] But rate law 2 has failed, too, *e.g.*, in certain halogenations of ketones, when $[OH^-] > 2[X_2]$ at high pH. Consequently, several mechanistic proposals concerning the slow step have been made, *e.g.*, hypohalite attacks the keto form,[7] hypohalite attacks the enol form,[8,9] or hypohalite attacks the enolate ion.[5,8] Only the last of these for the reaction of chlorine with acetone or acetophenone at high pH involves a rate law analogous to eq 3. Recognition[5,8] and revival of this rate law has some interesting and important consequences.

Three factors may contribute to the incursion of the third-order rate law. First, the weaker the carbon acid, the closer to the encounter rate will be the reaction of carbanion (C^-) with water, *e.g.*, k_{-6}. Second, at high pH, $[OX^-] >>> [X_2]^2$, and the presumably fast reaction of X_2 with C^- is negligible. Third, chlorine is "slow"; judging from the large gap in our hypobromite and hypochlorite rates, it is conceivable that in reactions with iodine or bromine or chlorine at high pH, a given carbon acid may follow either eq 2 or 3, or perhaps both. Thus, in a series of papers on the base-catalyzed reactions of 2-butanone, Rappe has reported variations in reaction rates, *e.g.*, with halogen or deuterium uptake, with pH, and with added salts.[7] In the high pH range, at least, we believe that eq 3 is consistent with his semiqualitative results.

Most halogenations, of course, follow eq 2. But certain important quantities, *e.g.*, pK values of weak carbon acids,[1a] deuterium isotope effects,[10] and tunneling in proton transfers,[11] have sometimes been determined by halogenation on the implicit assumption that mechanism 1 and eq 2 apply. Clearly, this is not always the case.

Further comments on these mechanistic problems will be made in the full paper.

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Sulfur-Containing Polypeptides. XI.
A Synthetic Route to Triscystine Peptides

Sir:

The sulfenyl thiocyanate method of disulfide synthesis[1] has been applied to the preparation of the cross-linked polypeptide VIII. The reaction sequence allows the stepwise introduction of each of the three disulfide bonds and may provide an unambiguous route to molecules of this type or other polypeptides containing several intrachain sulfur–sulfur bonds.

The A_{1-6} sulfur–sulfur bond in VIII was generated from the octapeptide derivative I by the action of thiocyanogen followed by hydrolysis with boron trifluoride etherate in acetic acid to produce the acid II in 67% overall yield.[2] Coupling of II with C-terminal tripep-

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