Thorium (*Concluded*)

Sample, g.	ThO_2, g.	Thorium, %
2.5011	.2131	7.49
2.0015	.1700	7.46
2.0550	.1762	7.52
	Average	7.50

Uranium

Sample, g.	$(UO_2)_2P_2O_7$, g.	Uranium, %
3.0044	0.0050	0.109
2.5011	.0038	.101
2.0015	.0033	.109
	Average	.106

Loss on ignition	0.838%
Loss at 110°, three hours	.14%

There were no indications of ordinary lead mineral associated with the sample. If we assume the absence of ordinary lead and make use of the conversion factor 0.36 for thorium, the lead–uranium ratio is

$$\frac{0.339}{0.106 + 0.36 \times 7.50} = 0.1208$$

The approximate age of the mineral is

$$\frac{0.121 \times 1.15 \text{ million years}}{1.57 \times 10^{-4}} = 886 \text{ million years}$$

With so old a mineral, the more exact or "logarithmic" formula for calculating age gives a materially different result from that found by the above "approximate" formula, and should be used in calculating the age of this material. Age, based on formula

$$\frac{\log(\mathrm{U} + 0.36\mathrm{Th} + 1.155\mathrm{Pb}) - \log(\mathrm{U} + 0.36\mathrm{Th})}{6.6 \times 10^{-5}} \text{ million years} = 858 \text{ million years}$$

As a pilot analysis for this work, Hecht made a complete microanalysis of a small piece from the crystal in Dr. Lane's possession. His results show, 9.36% thorium, 0.392% lead and give no figures for the uranium. Hecht obtains an age of 800 million years from his determination.

Acknowledgment.—The author is grateful to Mr. Rufus C. Little for the samples; to the Geological Society of America for financial assistance in part, for this research; to Dr. A. C. Lane for his constant interest in this work with helpful suggestions; and to the late Dr. Herman Schlundt and the University of Missouri for the use of the laboratories and other facilities.

Summary

This monazite is not a suitable source for pure "thorium-lead," as the analysis shows evidence of 0.106% uranium. The other analytical results are, 7.50% thorium and 0.339% lead. The age of the monazite is 858 million years, placing it in the Pre-Cambrian Age. Hecht, from his pilot analysis, obtains an age of 800 million years. It is probable but by no means certain that this material and the material Hecht used in his analysis came from the same deposit.

LAS VEGAS, N. M. RECEIVED AUGUST 22, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, LYNCHBURG COLLEGE]

The Effect of the Triple Bond on the Rate of Reaction of ω-Chlorides with Potassium Iodide in Absolute Acetone

BY M. J. MURRAY

Conant and his students[1] have studied the rates of reaction of a variety of organic chlorides with potassium iodide in absolute acetone. The only triple bond compound they reported on, however, was $CNCH_2Cl$. Truchet[2] has shown qualitatively that chlorine attached directly to a triple bond carbon is very unreactive toward sodium iodide in acetone.

The present investigation was made because no study has been reported showing the effect of the acetylenic linkage on the reactivity of chlorine in the ω-position. The series selected was $C_6H_5C{\equiv}C(CH_2)_nCl$, all members of which were prepared from phenylacetylene. Cinnamyl chloride was available for comparison of the effect of the ethylenic linkage.

The method of measuring the velocity of the reaction and of calculating the constant for the reaction was essentially that given in detail by Conant and students.

The results are summarized in Table I. It is seen that in this series of acetylenic chlorides there is a definite alternation of reactivity, the order with respect to the triple bond being $\alpha > \gamma > \beta$. This order of reactivity is the same as that found

---

(1) (a) Conant and Kirner, THIS JOURNAL, **46**, 232 (1924); (b) Conant and Hussey, *ibid.*, **47**, 476 (1925); (c) Conant, Kirner and Hussey, *ibid.*, **47**, 488 (1925).

(2) Truchet, *Ann. chim.*, [10] **16**, 309 (1931).

by Conant and Kirner[1a] for the simple C_6H_5 series without the triple bond ($C_6H_5CH_2Cl$, $K_{50} = 8.07$ > $C_6H_5CH_2CH_2CH_2Cl$, $K_{50} = 0.0713$ > $C_6H_5CH_2CH_2Cl$, $K_{50} = 0.0466$).

The inactivity of the chlorine attached to the triple bond carbon verifies Truchet's qualitative experiment and is to be expected in the light of the similar behavior of chlorine attached to an ethylenic carbon. Although chlorine α to a triple bond has somewhat smaller reactivity than when α to a double bond in the example studied, the order of activity is the same. The effect of the phenyl group in the 1-position can be evaluated approximately by the comparison of the values of the constants for allyl chloride[1c] and for cinnamyl chloride. It is apparent that the phenyl group extends its influence quite markedly by raising the value of the constant from 0.288 to 5.0. The effect of geometrical isomerism has not been studied, as only the *trans* form, cinnamyl chloride, was available.

TABLE I

REACTION VELOCITIES OF ω-CHLORIDES WITH POTASSIUM IODIDE IN ABSOLUTE ACETONE

Compound	K_{25}	K_{60}	Relative reactivity at 60°
$CH_3CH_2CH_2CH_2Cl$[1]	...	0.101	1
$C_6H_5C{\equiv}CCl$	...	0	0
$C_6H_5C{\equiv}CCH_2Cl$[a]	2.9	(79)	(782)
$C_6H_5C{\equiv}CCH_2CH_2Cl$	...	.048	0.48
$C_6H_5C{\equiv}CCH_2CH_2CH_2Cl$	...	.19	1.9
$C_6H_5CH{=}CHCH_2Cl$[a]	5.0	(138)	(1370)
$CH_2{=}CHCH_2Cl$[1]	0.288	(7.9)	(78)

[a] The values for K_{60} were calculated from the equation

$$\log \frac{K_{60}}{K_{25}} = 4000\left(\frac{1}{298} - \frac{1}{333}\right)$$

Experimental

Phenylethynyl Chloride (2-Chloro-1-phenylethyne).—This substance was prepared from sodium phenylacetylide and *p*-toluenesulfonyl chloride by the method of Truchet.[2] As he noted, phenylethynyl chloride begins to turn yellow very soon following distillation. After a few months, a sample of 9 g. yielded on distillation only 2 g. of the compound. Colorless crystals were found in contact with the viscous, dark brown resin. This resinification sets in so quickly that the first experiment carried out to determine the reaction velocity of this compound was misleading. The experiment was not started until three days after distillation of the chloride. As soon as the potassium iodide–acetone solution came into contact with the slightly yellow chloride, there was a gradual darkening of the solution; and after a short time a precipitate of potassium chloride began to form. At the end of seventeen hours the reaction was stopped, and titration showed that about 15% of the potassium iodide had disappeared. When the experiment was repeated immediately after distillation of the compound, the solution remained practically colorless; and after forty hours at 60° the difference between the "blank" and the reaction mixture was too small to be significant.

Chloromethylphenylacetylene (3-Chloro-1-phenylpropyne-1).—The compound was prepared by the action of phosphorus trichloride on phenylpropargyl alcohol in the presence of pyridine and ether. Tchao[3] prepared the corresponding bromide in an analogous way, using phosphorus tribromide. Into a flask containing 13.8 g. of phenylpropargyl alcohol dissolved in 10 ml. of dry ether and 1 ml. of pyridine, was slowly dropped 6.6 g. of phosphorus trichloride. The mixture was refluxed for two hours. A large volume of water was poured in, the layers separated, and the water extracted with ether. The ether layers were combined and washed with sodium bicarbonate solution, then with water, and dried over calcium chloride. The ether was driven off and the liquid distilled *in vacuo*. There was obtained 8 g. (51% yield) of purified product, b. p. 99° (7 mm.); $d^{20}{}_{20}$ 1.112, $n^{20}{}_D$ 1.5834.

Anal. Calcd. for C_9H_7Cl: Cl, 23.6. Found: Cl, 23.8.

Because of its great activity the reaction velocity of this compound was determined at 25° rather than at 60°.

β-Chloroethylphenylacetylene (4-Chloro-1-phenylbutyne-1).—This compound was prepared from the directions given by Johnson, Schwartz, and Jacobs:[4] b. p. 99° (3 mm.); $d^{20}{}_{20}$ 1.085.

Anal. Calcd. for $C_{10}H_9Cl$: Cl, 21.6. Found: Cl, 21.5.

When the reaction velocity is as low as in the case of this compound, a saving in time can be effected by weighing the chloride directly into the reaction tube, adding the acetone–potassium iodide solution, sealing the tube at once, and placing it in the bath as soon as possible. The accuracy of estimating the time of starting is considerably greater than that of titration. The latter, according to Conant and Kirner,[1a] is subject to a variation of ±4%.

γ-Chloropropylphenylacetylene (5-Chloro-1-phenylpentyne-1).—This compound also was prepared according to the method given by Johnson, Schwartz, and Jacobs:[4] b. p. 125° (6 mm.); $d^{20}{}_{20}$ 1.064.

Anal. Calcd. for $C_{11}H_{11}Cl$: Cl, 19.9. Found: Cl, 19.7.

Cinnamyl Chloride (3-Chloro-1-phenylpropene-1).—Eastman product redistilled, b. p. 106° (10 mm.).

Because the cinnamyl iodide, formed by the action of potassium iodide on cinnamyl chloride, liberates iodine during the titration of potassium iodide with potassium iodate in strongly acid solution, it is necessary to extract the mixture to be titrated before adding the potassium iodate. The liberation of iodine by cinnamyl iodide is especially rapid in sunlight but takes place too rapidly even in weak artificial light to permit titration without extraction.

All the chlorides were purified by distillation through a heated column 30 cm. long, packed with a spiral of No. 20 wire. A reflux ratio of at least 10 was used.

Acknowledgments.—This work was supported in part by a grant-in-aid from the Virginia Academy of Science from funds allotted it by the American Association for the Advancement of

---

(3) Tchao, *Bull. soc. chim.*, [4] **53**, 1533 (1933).

(4) Johnson, Schwartz, and Jacobs, THIS JOURNAL, **60**, 1882 (1938).

Science. The writer wishes to thank Dr. John R. Johnson not only for suggesting the investigation but also for helpful advice.

Summary

1. The reaction velocity of a series of acetylenic chlorides has been measured according to the method of Conant.

2. A definite alternation in reactivity has been observed.

3. The most active acetylenic chloride measured has a somewhat lower activity than the corresponding ethylenic compound.

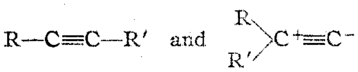
LYNCHBURG, VA. RECEIVED AUGUST 26, 1938

[CONTRIBUTION FROM THE CHEMICAL AND PHYSICAL LABORATORIES, LYNCHBURG COLLEGE]

Raman Spectra of Acetylenes. I. Derivatives of Phenylacetylene, $C_6H_5C{\equiv}CR$

BY M. J. MURRAY AND FORREST F. CLEVELAND

The Raman spectra of disubstituted acetylenes have been investigated by various workers, who have found that the characteristic acetylenic frequency in the region 2200–2300 cm.$^{-1}$ is usually double or triple, although in a few cases it is reported as a single, broad line.[1] Several explanations of this splitting have been given: Glockler and Davis[2] attribute the two strong lines in dimethylacetylene to symmetrical and asymmetrical vibrations. Gredy[3] suggests, as a working hypothesis, that two isomeric forms



$$R{-}C{\equiv}C{-}R' \quad \text{and} \quad {}^{R}_{R'}\!\!>\!C^{+}{\equiv}C^{-}$$

may exist simultaneously. Kohlrausch, Pongratz and Seka[4] regard the existence of two or more frequencies, if only one molecular form is present, as difficult to understand. Badger[5] attributes the doubling to a Fermi resonance interaction between the fundamental acetylenic frequency in this region and an overtone of a lower frequency near 700 or 1100 cm.$^{-1}$.

Gredy[3] found two lines for $C_6H_5C{\equiv}CCH_2OH$, while Faucounau[6] reported a single broad line for $C_6H_5C{\equiv}CCH_2CH_2OH$, and Bourguel and Daure[7] only a single frequency for $C_6H_5C{\equiv}CCl$. In view of these results and of the difference in opinion as to the cause of the splitting, it appeared worth while to investigate carefully the Raman spectra of disubstituted acetylenes in order to determine how the nature of the splitting varies for closely related molecules and to determine, if possible, whether there is a certain kind of substitution that yields only a single frequency. The present paper gives the results obtained for a series of compounds of the type $C_6H_5C{\equiv}CR$.

Experimental Procedure

The apparatus and experimental technique were essentially the same as previously described.[8] All the compounds were purified carefully by distillation in a heated column, using a high reflux ratio. Since the acetylenic compounds suffered photochemical decomposition when exposed to the exciting light and since the decomposition products were fluorescent and added greatly to the continuous background, it was necessary to redistill, from a flask attached to the scattering tube, at one-hour intervals during the exposures. In spite of these precautions, the continuous background was strong, especially in the case of the bromide.

The general procedure was to obtain several plates with both long and short exposure times, using both Hg 4047 Å. and 4358 Å. for excitation. The more intense lines could be measured with greater accuracy on the short exposure plates. In order to secure better definition of the stronger lines, the camera lens was stopped down to 5 mm. and a final exposure made. The time of this exposure was ten hours. The lines on these plates were exceedingly sharp and the acetylenic frequency in the 2200 cm.$^{-1}$ region, which on the other plates appeared as a single broad line, was resolved.

The comparator was illuminated with light from a yellowish-brown incandescent lamp, a practice which resulted in increased distinctness for the weaker lines.

Results

The results are given in the sections below, in which k, f, and e represent excitation by Hg 4047, 4347, and 4358 Å., respectively. Broad lines are designated by b and estimated intensities are given by the numbers in parentheses.

---

(1) James H. Hibben, *Chem. Rev.*, **18**, 50-51 (1936).

(2) G. Glockler and H. W. Davis, *J. Chem. Phys.*, **2**, 881 (1934).

(3) Blanche Gredy, Thèses, Paris, 1935.

(4) K. W. F. Kohlrausch, A. Pongratz and R. Seka, *Sitzber. Akad. Wiss. Wien.*, Abt. IIb, **146**, 218 (1937).

(5) Richard M. Badger, *J. Chem. Phys.*, **5**, 178 (1937).

(6) Louis Faucounau, *Compt. rend.*, **199**, 605 (1934).

(7) M. Bourguel and P. Daure, *Bull. soc. chim.*, **47**, 1349 (1930); *Compt. rend.*, **190**, 1298 (1930).

(8) Forrest F. Cleveland and M. J. Murray, *Am. Phys. Teacher*, **5**, 270 (1937).