There also seems to be indicated a dependence of activity on the lattice constant of the catalyst. However, we feel that the present meager data do not warrant any detailed discussion at the present time.

Summary

A series of pure single metal catalysts and pure mixed metal catalysts have been prepared under similar conditions. The activity of each of the catalysts has been determined for the hydrogenation of benzene to cyclohexane. The crystal structure of each of the catalysts has been determined by x-ray diffraction studies.

The structure investigations show that the substitutional type of solid solution is formed during the reduction of the mixed oxides to the mixed metal catalyst. The lattice types and the lattice constants of the mixed metals are dependent on the composition of the mixture and on the lattice types and lattice constants of the components.

It has been shown that a relationship exists between the arrangement of the metal catalyst atoms in the crystal and the activity of the catalyst.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Dielectric Properties of Acetylenic Compounds. II. The Electric Moments of Some Alkyl Halogenoacetylenes

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Because of the peculiar chemical properties of the halogen in acetylenic halides, it was thought that the electric moments of these compounds might exhibit a marked variation from those of the corresponding alkyl halides. *n*-Butyl and *n*-amyl halogenoacetylenes were chosen, as inductive effects would not ordinarily be expected to cause appreciable difference in moment between hydrocarbon chains of four and five carbon atoms, and the moments would serve as a check on one another.

The following compounds were used: 1-chloro-, 1-bromo- and 1-iodoheptyne-1, and 1-chloro-, 1-bromo- and 1-iodohexyne-1.

Preparation

The chloro derivatives of hexyne-1 and heptyne-1 were prepared by the reaction between benzene sulfonyl chloride and the sodium salt of hexyne-1 or heptyne-1, the reaction being carried out in ethyl ether.[1]

1-Chloro-1-heptyne, b. p. 65° at 49 mm.
1-Chloro-1-hexyne, b. p. 47° at 55 mm.

The bromo compounds were prepared by stirring hexyne-1 or heptyne-1 with an alkaline solution of potassium hypobromite.[2] An efficient, high-speed motor stirrer caused proper emulsification, rendering unnecessary the addition of potassium stearate or stearic acid.

1-Bromo-1-heptyne, b. p. 54.5° at 10.5 mm.
1-Bromo-1-hexyne, b. p. 38° at 15 mm.

The iodo compounds were prepared by the direct iodination of the sodium butyl or amyl acetylide in liquid ammonia, according to the method given by Vaughn and Nieuwland.[3]

1-Iodo-1-heptyne, b. p. 93° at 21 mm.
1-Iodo-1-hexyne, b. p. 75° at 20 mm.

All the compounds were purified by distillation under reduced pressure through an all-glass apparatus, using a 38-cm. spiral fractionating column. The fractions used varied less than 0.5° in boiling point. The stability of these compounds decreases from the chlorides to the iodides, the latter developing a pink color in twenty-four hours or less, even when kept in the dark and cold. Very slight decomposition was sufficient to cause wide variations in the dielectric constant. Freshly prepared and distilled samples were used, to minimize errors from this effect.

Experimental

All measurements of dielectric constant and density were made in benzene solution at 25°. The dielectric constant was determined by the use of the modified heterodyne beat method, as described by Otto and Wenzke.[4] Refractive indices were measured by means of a Pulfrich refractometer.

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

[2] Straus, Kollek and Heyn, *Ber.*, **63B**, 1868 (1930).

[3] Vaughn and Nieuwland, THIS JOURNAL, **55**, 2150 (1933).

[4] Otto and Wenzke, *Ind. Eng. Chem., Anal. Ed.*, **6**, in press (1934).

The variation of dielectric constant and density with concentration is shown in Table I.

TABLE I

c_2	d	ϵ
1-Chloro-1-heptyne		
1.0000	0.9110	...
0.1015	.8771	2.466
.0740	.8760	...
.0700	...	2.404
.0494	.8745	2.370
.0264	.8734	2.327
1-Chloro-1-hexyne		
1.0000	0.9205	...
0.0745	.8762	2.408
.0561	.8751	2.374
.0386	.8736	2.346
.0375	.8741	2.342
1-Bromo-1-heptyne		
1.0000	1.2077	...
0.1219	0.9331	...
.0848	...	2.380
.0821	.9136	2.377
.0744	.9100	...
.0656	...	2.356
.0206	.8839	2.302

c_2	d	ϵ
1-Bromo-1-hexyne		
1.0000	1.2529	...
0.0914	0.9191	2.397
.0786	...	2.381
.0752	.9115	...
.0565	.9020	2.351
.0387	.8925	2.327
.0377	.8914	...
1-Iodo-1-heptyne		
1.0000	1.4726	...
0.0997	...	2.350
.0789	0.9461	2.336
.0649	.9330	...
.0646	...	2.324
.0487	.9178	2.315
.0307	.9020	...
.0128	.8840	2.285
1-Iodo-1-hexyne		
1.0000	1.5543	...
0.0808	0.9506	2.338
.0629	.9338	2.323
.0464	.9179	2.311
.0218	.8938	2.293

Values of refractive index, molecular refraction, slope of the curve P_{12} *vs.* concentration at infinite dilution, and polarization of solute at infinite dilution, are given in Table II.

TABLE II

	n_D	MR_D	$(dP_{12}/dc_2)_{c_2=0}$	P_∞
1-Chloro-1-heptyne	1.43741	37.57	44.29	71.01
1-Chloro-1-hexyne	1.43350	32.93	37.31	64.02
1-Bromo-1-heptyne	1.46245	39.87	35.98	62.66
1-Bromo-1-hexyne	1.46295	35.36	31.78	58.58
1-Iodo-1-heptyne	1.50920	45.03	37.66	58.15
1-Iodo-1-hexyne	1.51510	40.36	25.39	52.09

Calculations of polarizations were made by the method of Hedestrand.[5]

Discussion

Table III includes the values of the dipole moments measured, together with those of other halides.

TABLE III

$\mu \times 10^{18}$

	1-Chloro	1-Bromo	1-Iodo
Heptyne-1	1.27	1.05	0.80
Hexyne-1	1.23	1.06	.75
Ethylene[6]	..	1.5	..
Propene-1[6]	1.7	..	..
Benzene[7]	1.52	1.50	1.25
Heptane[7]	1.85	1.84	1.84

The comparison shows a rough decrease in moment of organic halides of the RX type as R changes from alkyl to aryl to ethylenic to acetylenic groups.

Acetylenic halides have in the past been said to contain "positive halogen" because of their anomalous chemical properties. The values of dipole moment for these compounds show that, while there is a considerable decrease in polarity due to the presence of the triple bonded group, the direction of the carbon–halogen dipole is the same as that which obtains in the other organic halides.

Summary

1. The dipole moments of a number of alkyl halogeno-acetylenes have been measured.

2. These moments indicate that the carbon to halogen linkage decreases in polarity as the carbon becomes less saturated.

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(5) Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).

(6) Bergmann and Engel, *Z. physik. Chem.*, **B8**, 111 (1930).

(7) Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., Inc., New York, 1931.