two possible mechanisms for a reaction, each involving the configurations of different numbers of electrons, the one involving the configuration of the smaller number of electrons will possess the smaller activation energy. In other words, a given reaction will occur in such a way as to make and break as few bonds as possible. Another example is given by Kimball and Eyring.[28]

Some of the predictions made in this communication are to be tested experimentally in this Laboratory.

We wish to thank Professor Daniels for many valuable discussions.

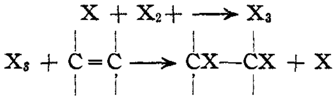
Summary

Activation energy calculations have been made for various reactions involved in the possible modes of decomposition of the ethylene halides. On the basis of these calculations one is led to expect:

1. Ethylene iodide will decompose homogeneously in the gas phase by the simultaneous operation of two mechanisms, a unimolecular decomposition, and an atom catalyzed reaction, but ethylene chloride will only decompose by the atom catalyzed reaction. Ethylene bromide is intermediate between ethylene iodide and ethylene chloride and one cannot safely predict whether it will behave like the iodide or like the chloride compound.

2. Ethylene iodide will decompose homogeneously in the gas phase at an appreciable rate at a lower temperature than ethylene bromide, which in turn will decompose at a lower temperature than ethylene chloride.

3. The type of chain proposed by Purakayastha and Ghosh is unsatisfactory. The diatomic halogen molecule will add to the double bond more rapidly than the triatomic molecule.



$$X + X_2 + \longrightarrow X_3$$

$$X_3 + \overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}} \longrightarrow \overset{|}{\underset{|}{C}}X-\overset{|}{\underset{|}{C}}X + X,$$

MADISON, WISCONSIN RECEIVED FEBRUARY 23, 1934

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[28] Kimball and Eyring, THIS JOURNAL, **54**, 3876 (1932).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

The Activity and Crystal Structures of Mixed Metal Catalysts[1]

BY J. H. LONG, J. C. W. FRAZER AND EMIL OTT

Introduction

It has been suggested that gaseous reactions which are catalyzed by solid surfaces should be sensitive to the arrangement of and the distance between the surface atoms.[2] Unfortunately, too little experimental evidence on the structure of crystalline catalysts has been advanced to support these views. However, it has been shown that the course of decomposition of methanol is influenced by the shift in the crystal structure of zinc oxide–copper catalysts.[3] It also has been shown that the energy of activation for the reaction between carbon monoxide and oxygen is influenced by the lattice dimensions of an alumina–ferric oxide catalyst.[4] Other work,[5,6] in which catalyst structure investigations were not carried out, indicates a dependence of catalytic activity on lattice type and lattice dimensions.

In view of the above, it was deemed advisable to continue this line of investigation. If a relationship does exist between the activity of a catalyst and the distance between and the arrangement of the surface atoms, such phenomena should become observable when the arrangement of the atoms of the underlying material is actually altered. By preparing the substitutional type of solid solution, the lattice constants and the lattice types of mixtures of iron, nickel, cobalt and copper can be varied in a systematic manner. Four series of mixed metal catalysts have been prepared under identical conditions. The structures of the catalysts have been determined by x-ray diffraction studies. The activities of the mixed metal and single metal catalysts have been determined by observing their relative effect in promoting the reaction between hydrogen and benzene to form cyclohexane.

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[1] From the thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy by J. H. Long. Presented in part at the 1933 Washington meeting of the American Chemical Society, by E. Ott.

[2] Langmuir, *Trans. Faraday Soc.*, **17**, 617 (1921); Balandin, *Z. physik. Chem.*, **B2**, 289 (1929).

[3] Frolich, Fenske and Davidson, *Ind. Eng. Chem.*, **21**, 109 (1929).

[4] Eckell, *Z. Elektrochem.*, **38**, 918 (1932).

[5] Kahlenberg and Ritter, *J. Phys. Chem.*, **25**, 89 (1921).

[6] Remy and Schaefer, *Z. anorg. allgem. Chem.*, **136**, 149 (1924).

Experimental

Preparation of Catalysts.—The single or mixed metal hydroxides were precipitated by adding slowly a one molar solution of sodium hydroxide to a one molar solution of the metallic nitrate (or nitrates) at 90° with rapid agitation. After cooling to room temperature, washing by decantation, and peptizing the precipitate, the sodium nitrate was effectively eliminated from it by electrodialysis,[7] after which it was dried at 115° and made into pills.

After use in the hydrogenation apparatus, the catalysts were analyzed; for copper and cobalt electrolytically, for nickel electrolytically or by precipitation with dimethylglyoxime, and for iron by the Zimmermann–Reinhardt method.[8]

Testing of Catalyst Activity.—A flow of electrolytic hydrogen, measured by a calibrated flowmeter, was purified in the usual manner by passing the gas over a platinized asbestos catalyst and then over sodium hydroxide and phosphorus pentoxide. The purified hydrogen could be either bubbled into or by-passed around three benzene saturators, which were placed in series. The benzene used was carefully purified.[9]

The first benzene saturator was held at 25° while the others were maintained at 20.4 (±0.05°) by a water thermostat. At 20.4° and one atmosphere pressure, the vapor pressure of benzene[10] is such that the ratio of hydrogen to benzene is 9 to 1. Departures from this ratio caused by the usual fluctuations in the atmospheric pressure, did not have a measurable effect on the percentage conversion to cyclohexane.

The mixture of benzene and hydrogen entered the catalyst testing chamber, which was maintained at the desired temperature by either an oil or a water bath. An electric furnace, constructed so as to have a minimum temperature gradient in the region of the catalyst bed, was used to obtain the higher temperatures necessary for reduction of the oxides to the active catalysts.

The reaction products leaving the catalyst chamber entered a condenser, from which condensates were collected every ten minutes for analysis. The analyses were determined by refractive index measurements.

A curve was constructed by plotting the molar composition of known benzene–cyclohexane mixtures against their observed refractive index. The refractive index and hence the composition of an unknown mixture of the condensate then could be determined rapidly with an accuracy of better than 0.15 mole per cent. at ten to fifteen minute intervals.

A 5-cc. charge of the single metal oxide or mixed metal oxides was reduced according to a definite reduction schedule. Hydrogen was bypassed around the benzene saturators at a flow of 108 cc. per minute to the catalyst bed. The temperature of the catalyst bed was raised to 200° in one hour and then raised 25° every thirty minutes until 450° was reached. After holding the temperature at 450° for an additional hour, the catalyst was cooled to room temperature. The stream of hydrogen was then turned into the benzene saturators and the activity of the catalyst was tested. Each catalyst was tested for several hours at a given temperature after a steady state of activity was achieved. Since the tests extended over several days, the catalyst was protected in an atmosphere of hydrogen when the tests were interrupted. At the end of the regular reduction and testing period, some of the catalysts were reduced for an additional length of time at 450°. This was done in order to determine as closely as possible the maximum activity of the catalyst as a function of the time of reduction at 450°.

Two typical examples of such catalyst activity studies are given in Tables I and II.

Table I

Catalyst composition, 45.4% Co, 54.6% Ni; catalyst volume, 2 cc.; reduction: regular 7 hour schedule + 1 hr. at 450°; ratio of H_2 to C_6H_6: (a) 9 to 1, (b) 8.5 to 1, (c) 9.5 to 1.

Temp., °C.	60 (a)	71	80	90	80
Conv., %	26.7	57.4	80.0	91.4	76.5
Temp., °C.	91	70	45	90	100
Conv., %	90.2	50.3	9.0	89.0	93.2
Temp., °C.	100 (b)	100 (a)	100 (c)	100 (a)	80	50
Conv., %	92.0	94.1	95.2	93.6	75.8	13.2

Table II

Catalyst composition, 25.1% Fe, 74.9% Co; catalyst volume, 2.6 cc.; reduction: regular schedule + 4 hrs. at 450°.

Temp., °C.	86	100	91	80	71
Conv., %	67.0	91.9	75.8	45.6	16.3
Temp., °C.	57	100	60	75	81
Conv., %	7.8	88.0	7.4	24.3	50.8

(Reduction beyond the given times gives decrease in activity; the times given yield the optimum catalytic activities.)

x-Ray Determination of Crystal Structure.—After the completion of an activity test, the catalyst was discharged from the hydrogenation apparatus and ground to a fine powder in an agate mortar. It was then intimately mixed with an equal weight of very pure pulverized sodium chloride (Kahlbaum "for analysis with a certificate of guarantee"). The co-powdered crystals were packed into thin-walled collodion tubes of an internal diameter of 0.4–0.5 mm. The use of sodium chloride for the exact determination of lattice spacings has been described, for instance, by Wyckoff.[11] The lattice constant of pure sodium chloride was taken to be 5.6280 Å.[12] The sample in its collodion tube was then centered in a camera of the Debye–Scherrer type having an effective diameter of 114.6 mm. The source of radiation was a Seeman–Hadding ionic type of x-

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(7) Bennett, Dissertation, The Johns Hopkins University, 1930.

(8) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York.

(9) Dietz, Dissertation, The Johns Hopkins University, 1932.

(10) Déjardin, *Ann. Physik*, [9] **11**, 253 (1919).

(11) Wyckoff, "The Structure of Crystals," The Chemical Catalog Co., Inc., New York, 1931.

(12) Ewald and Hermann, "Strukturbericht," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1931.

ray tube with a chromium target. The tube was operated at 30–35 kv. and 20 ma., the Kα and Kβ radiations being used for the diffraction studies. Some of the investigations were carried out using a hot-filament tube (Seeman design) for the production of Cu Kα radiation. The Cu Kβ radiation was practically completely absorbed by a thin nickel foil, 0.02 mm. thick, which was placed between the source of radiation and the camera slit.

Each diffraction pattern was measured at least six times with a ruler and from the average values the lattice constant of the catalyst material was determined accurately according to standard methods, making use of the presence of the sodium chloride diffractions for calibration purposes. In some cases it was possible to measure the films with a Gaertner micro-comparator. However, such results were identical, within the limit of error, with results obtained above.

To illustrate the accuracy of the procedure two typical examples are given in Tables III and IV.

TABLE III

Composition of catalyst (75.8% Fe–24.2% Co); radiation, Cr-Kα + β.

(*hkl*)	*I*	Diffracting material	*L*	Θ (corrected)	a_0
200	w.	NaCl	87.25		
200	m.-s.	NaCl	96.37		
110	m.	Catalyst	124.25	31.012	2.856_6
220	w.	NaCl	126.28		
110	v.s.	Catalyst	138.23	34.478	2.856_2
220	s.	NaCl	140.62		
222	v.w.	NaCl	159.48		
222	m.	NaCl	178.85		
200	w.	Catalyst	187.06	46.790	2.855_7
400	v.w.	NaCl	....		
200	s.	Catalyst	212.68	53.242	2.854_1
400	m.	NaCl	217.07		
420	m.	NaCl	222.90		
211	m.s.	Catalyst	252.55	63.222	2.855_4
420	v.s.	NaCl	260.80		

Lattice constant, a_0 = 2.855_6 Å. (The average deviation from the mean value of a_0 is ±0.000_7 Å.) Lattice type: body-centered cubic.

Results and Discussion

A summary of the results on the composition, structure and relative activity of each of the different single metal and mixed metal catalysts is given in Table V. The relative activities of the catalysts referred to in this table are arbitrarily defined in terms of the temperatures at which the catalysts produce a 10, 50 and 90% conversion of hydrogen and benzene to cyclohexane. These temperatures were found from a plot of the observed percentage conversions against the different testing temperatures.

TABLE IV

Composition of catalyst (79.0% Cu–21.0% Ni); radiation, CuKα.

(*hkl*)	*I*	Diffracting material	*L*	Θ (corrected)	a_0
200	s.	NaCl	63.84		
111	v.s.	Catalyst	87.32	21.794	3.595_2
220	m.	NaCl	91.21		
200	s.	Catalyst	101.57	25.379	3.595_5
222	m.	NaCl	113.22		
400	w.	NaCl	132.71		
220	s.	Catalyst	148.93	37.399	3.596_6
420	s.	NaCl	150.82		
422	m.	NaCl	168.08		
311	v.s.	Catalyst	180.78	45.327	3.593_0
222	m.	Catalyst	191.20	47.952	3.594_3
440	w.	NaCl	202.30		
600 442	m.	NaCl	220.75		
400	w.	Catalyst	235.05	59.003	3.595_5
620	m.	NaCl	238.92		
622	m.	NaCl	259.80		
331	s.	Catalyst	275.11	69.080	3.595_6

Lattice constant, a_0 = 3.595_1 Å. (The average deviation from the mean value of a_0 is ±0.000_8 Å.) Lattice type: face-centered cubic. In these two tables, *L* is the measured distance in mm. between corresponding lines on the film. The intensity, *I*, of the diffraction is designated by v.w. = very weak, w. = weak, m. = medium, s. = strong and v.s. = very strong.

TABLE V

Catalyst composition, %	Temp., giving a conversion of 10%	50%	90%	Lattice type	Lattice constant (Å.)	Remarks
100 Ni	53	66	72	f.c.c	3.5154 ± 0.0006	
100 Fe				b.c.c.	2.8602 ± 0.0007	[a]
100 Co		43	61	f.c.c	3.5343 ± 0.0010	Predominant
				h.c.p.		[b]
100 Cu				f.c.c.	3.6059 ± 0.0005	[c]
74.7 Ni–25.3 Fe	90	108	126	f.c.c.	3.5430 ± 0.0007	
49.1 Ni–50.9 Fe	93	120	131	f.c.c.	3.5615 ± 0.0009	
24.1 Ni–75.9 Fe	100	129	149	f.c.c.	3.5837 ± 0.0009	
				b.c.c.	2.8623 ± 0.0006	Predominant
76.4 Ni–23.6 Co	50	73	86	f.c.c.	3.5209 ± 0.0008	
54.6 Ni–45.4 Co	48	69	87	f.c.c.	3.5243 ± 0.0007	
28.4 Ni–71.6 Co			87	f.c.c.	3.5295 ± 0.0011	
71.8 Ni–28.2 Cu	119	148	161	f.c.c.	3.5386 ± 0.0006	
46.4 Ni–53.6 Cu	91	115	126	f.c.c.	3.5646 ± 0.0008	
21.0 Ni–79.0 Cu	90	111	126	f.c.c.	3.5951 ± 0.0008	
75.8 Fe–24.2 Co				b.c.c.	2.8556 ± 0.0007	[d]
50.0 Fe–50.0 Co				b.c.c.	2.8506 ± 0.0008	[e]
25.1 Fe–74.9 Co	63	80	98	b.c.c.	2.8400 ± 0.0010	Predominant
				f.c.c.	3.5441 ± 0.0007	

[a] The iron catalyst was inactive at all testing conditions. [b] The diffractions from the hexagonal close-packed lattice of cobalt were too weak to permit an accurate determination of the lattice constant. [c] The copper catalyst was inactive. [d] The catalyst was inactive at all testing conditions. [e] The activity of this catalyst was not constant.

It has been demonstrated by others that the activity is dependent to some extent on the size of the crystalline catalyst particles. Scherrer and others[13] have shown that the line width of the x-ray diffractions from powdered crystals is a function of the particle size of the diffracting material. An inspection of the different diffraction photographs showed that the line widths are of comparable dimensions. Also, inasmuch as the crystal size is such as to give the maximum sensitivity of the above method, the large differences in the observed activities of the catalysts cannot be due to differences in the particle size of the catalyst crystals.

It also is well known that the activity is dependent on the purity of the catalyst and on the purity of the testing materials. The exceptionally high conversions obtained with some of the catalysts can be taken to indicate that the testing materials, *i. e.*, the hydrogen and benzene, were pure. The activities also were found to be reproducible and this rules out the possibility of occasional poisons. It therefore follows that the difference observed in the activities cannot be ascribed to impurities in the hydrogen and the benzene. Furthermore, it is unlikely that the systematic variations in the activities are due to traces of poisons in the catalysts. This is, of course, further emphasized by the fact that all the catalysts were of highest purity and that all of the catalysts were prepared according to the same principles.

Differences in the testing conditions would be expected to influence the percentage conversion of hydrogen and benzene to cyclohexane. However, the percentage conversion was not affected appreciably when purposely made departures of several times the magnitude of the possible normal experimental variations were made. Inconstancy of testing conditions cannot be advanced to explain the variations in the activity of this series of catalysts.

It is recognized that the activity of a metal catalyst, prepared by reduction from the oxide, is dependent on the time and temperature of the reduction. The different single metal oxides and the mixed metal oxides no doubt have a time and temperature of reduction which would produce a catalyst of even higher activity than that found in these studies. The search for this optimum condition of reduction for each of the catalysts was outside the interest of this work. However, the maximum activity of the catalysts at a temperature of reduction of 450° was found by reducing the catalyst for different periods of time at this temperature. Our results indicate that only in the case of pure copper and the 71.8% Ni–28.2% Cu catalyst over-reduction has taken place by heating at 450° during the regular reduction schedule. The result with copper is in agreement with the work of Pease and Purdum,[14] who found that copper was only active for the hydrogenation of benzene if it were reduced carefully at low temperatures.

The results of the activity tests show that the single metal catalysts are sharply divided into two classes. Cobalt is slightly more active than nickel. Iron and copper are inactive in this reaction. It must be emphasized that the inactivity of iron is not due to insufficient reduction or over-reduction of the iron oxide. The x-ray diagrams of the discharged catalyst do not show any lines of iron oxide. Since the reduction of the iron oxide surface would precede the reduction of the oxide interior, it appears that the surface atoms of the iron catalyst were in a reduced state when the catalyst was in the hydrogenation apparatus. A catalyst of iron reduced as high as 500° was also inactive. Furthermore, it is unlikely that the inactivity of the iron is due to too high a temperature of reduction since most of the commonly known active iron catalysts for other hydrogenation reactions are prepared by reducing the oxide at temperatures of 500°. In view of the work of Pease and Purdum[14] it is concluded that the copper catalyst is over-reduced and cannot be compared with the other catalysts.

From the possible standpoint of dilution of the active constituents, the cobalt–iron catalysts would be expected to have the same activity as the nickel–iron catalyst of corresponding concentration. However, it is found that the 24.2% Co–75.8% Fe catalyst is entirely inactive while the 24.1% Ni–75.9% Fe catalyst is moderately active. Furthermore, in contrast to the moderate but strictly reproducible activity of the 49.1% Ni–50.9% Fe catalyst, the 50.0% Co–50.0% Fe catalyst exhibits a persistent erratic behavior. Numerous attempts to level off the irregular behavior of the cobalt–iron catalyst to a steady state are without success. Changes in the

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(13) See, for example, H. Ott, "Handbuch der Experimentalphysik," Akademische Verlagsgesellschaft m. b. H., Leipzig.

(14) Pease and Purdum, THIS JOURNAL, **47**, 1435 (1925).

testing condition and the time of reduction at 450° do not alter the random character of the activity.

The activity of the catalysts of the cobalt–nickel series is found to be higher than the activity observed for any of the other mixed metals. The 71.6% Co–28.4% Ni preparation is found to be more active than either the pure nickel or the pure cobalt catalysts. The other two members of this series are found to have activities of the same order of magnitude as that of pure nickel.

The more active copper–nickel preparations show a slight increase in activity after longer periods of reduction at 450° following the regular reduction and testing period. However, the 28.2% Cu–71.8% Ni catalyst shows a decrease in activity as the time of reduction exceeds the regular reduction period. Therefore, it is likely that the lowered activity of this catalyst is due to a "temperature of reduction" effect. Consequently this result and the one found with copper are not considered further.

The x-ray diffraction studies show that the iron crystallizes in its usual body-centered cubic lattice and that nickel and copper crystallize in their normal face-centered cubic lattices. The cobalt is found to have a face-centered cubic lattice and the usual hexagonal close packed lattice. The x-ray diffractions from the face-centered lattice of cobalt are more intense than the diffractions from the hexagonal close packed lattice. The observation confirms the studies of Masumato,[15] who found that a sample of cobalt prepared by reduction of the oxide in hydrogen was predominantly a face-centered modification.

The x-ray diffraction studies of the mixed metal catalysts show that the predicted substitutional type of solid solution is effected by the reduction of the co-precipitated oxides and that the lattice constants of these mixtures obey essentially Vegard's rule, as would be anticipated. The structure type is either cubic face- or body-centered, or both.

The body-centered cubic lattice constants of the iron–cobalt mixtures do not show linear dependence on the composition of the mixture. (However, this may only be apparent since the two phases may have different composition.) This result confirms the observations of Osawa[16] on the structure of iron–cobalt alloys.

A correlation of the results of the activity tests and the structure determinations offers an explanation for the apparently anomalous behavior of certain of the catalysts. An inspection of Table V demonstrates that the single metal and mixed metal catalysts which crystallize at least in part with face-centered cubic lattices are active, while those preparations which crystallize exclusively with the body-centered cubic lattice are inactive (or erratic) as catalysts for the hydrogenation of benzene.

For example, the iron catalyst is inactive and has a body-centered cubic lattice. The nickel and cobalt are active and have the face-centered cubic lattices.

When the mixed oxides of iron and nickel are reduced, the resultant catalyst is face-centered cubic and is active. When the mixed oxides of iron and cobalt are reduced, the 74.9% Co–25.1% Fe catalyst is active and it shows the presence of a face-centered cubic lattice. However, the other two members of the iron–cobalt series do not show any face-centered cubic lattice and they are inactive or else erratic in their behavior. It is not unlikely that the erratic behavior of the 50% Co–50% Fe mixture may be due to the presence of traces of an unstable face-centered arrangement of the surface atoms of the catalyst. The richer the mixture becomes with respect to the cobalt, the more probable it will be that the catalyst will have more of the face-centered cubic lattice and hence will be active.

The results show that the copper–nickel catalysts and the nickel–cobalt catalysts have face-centered cubic lattices and are catalytically active.

It must be emphasized that these results should not be taken to mean that a catalyst which has a face-centered cubic lattice will always be active for the hydrogenation of benzene. Other factors as, for example, the time and temperature of reduction will likewise affect the activity. However, it can be stated that, in view of these studies, the body-centered lattice type will be an inactive catalyst for this particular hydrogenation. For other catalytic hydrogenations, the body-centered lattice type may be active. This is concluded from some preliminary experiments which showed that the body-centered cubic iron and the body-centered cubic iron–cobalt catalysts are quite efficient in catalyzing the hydrogenation of ethylene.

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(15) Masumato, *Science Repts. Tôhoku Imp. Univ.*, **15**, 449 (1926).

(16) Osawa, *ibid.*, **16**, 109 (1927).

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.

BALTIMORE, MD. RECEIVED FEBRUARY 24, 1934

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

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

BY DANIEL J. PFLAUM AND HERMAN H. WENZKE

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).