Condensation of Isobutane with Vinyl Chloride

Procedure.—Vinyl chloride (80 g.) was bubbled during two hours into a well-stirred mixture of isobutane (340 g.) and aluminum chloride (30 g.), the apparatus being essentially that described above for the allyl chloride experiments. The temperature was that of the refluxing mixture (i. e., about -10 to $-8°$). The catalyst remained granular until about 80% of the vinyl chloride had been added; little hydrogen chloride was evolved. As the addition was continued, the catalyst began to coagulate and was gradually converted into a red liquid; more hydrogen chloride was evolved. Stirring was continued for ten minutes, after which the upper layer was decanted from the 31 g. of catalyst layer and stabilized. There were recovered 281 g. of butane and 121 g. of liquid product. The soda lime tower gained 4 g. Distillation of the washed liquid product yielded 19 g. of material boiling at $50-55°$ ($n^{20}D$ $1.376-1.380$; density, about 0.75) which consisted of approximately equal amounts of hexane and t-butyl chloride (identified as the anilide, m. p. 128°) and 44 g. of product boiling at $145-148°$ which consisted of 1,1-dichloro-3,3-dimethylbutane (of Fig. 2). There was also obtained about 15 g. of higher boiling compounds.

In another experiment, 8 g. of aluminum chloride, 80 g. of isobutane and 32 g. of vinyl chloride were weighed into a glass liner (cooled in a bath at $-78°$) for an Ipatieff-type rotating autoclave. The liner was sealed into the autoclave which was then rotated at room temperature four hours after which it was allowed to set overnight. The gaseous material was passed through a soda lime tower (which gained 7 g.) and was collected in a trap immersed in Dry Ice–acetone; 23 g. of condensable gas was obtained. The autoclave was opened and 61 g. of liquid product was separated from 22 g. of red-brown fluid catalyst, washed, dried, and distilled. There was obtained, besides paraffin hydrocarbons, about 8 to 10 g. of 1,1-dichloro-3,3-dimethylbutane contaminated with isoparaffin.

1,1-Dichloro-3,3-dimethylbutane.—The dichlorohexane boiled without decomposition at $146-147°$ at atmospheric pressure. It melted at -60 to $-59°$. Other physical properties: $n^{20}D$ 1.4370; d^{20}_4 1.0056; mol. ref.: calcd. for $C_6H_{12}Cl_2$, 39.6; obs., 40.3. *Anal.* Calcd. for $C_6H_{12}Cl_2$: C, 46.5; H, 7.75; Cl, 45.75. Found: C, 49.90; H, 8.15; Cl, 42.1. The presence of an impurity (paraffin or chlorohexane) is indicated.

Pure 1,1-dichloro-3,3-dimethylbutane prepared by the condensation of t-butyl chloride with vinyl chloride[3] has the following properties: b. p. 148-148°; m. p. -56.5 to $-56°$; mixed with above dichloride, m. p. -58 to $-57°$; $n^{20}D$ 1.4389; d^{20}_4 1.0262; mol. ref.: obs., 39.7. *Anal.* C, 46.70; H, 7.89; Cl, 45.08.

Proof of Structure of 1,1-Dichloro-3,3-dimethylbutane. —Heating the dichloroneohexane with water in a sealed tube at 300° yielded an aldehyde, b. p. 102-103°. The 2,4-dinitrophenylhydrazone and the dimedon derivative of the aldehyde melted at 146-147° and 162-163°, respectively, proving that the aldehyde was t-butylacetaldehyde.[11] The dichloride was, therefore, 1,1-dichloro-3,3-dimethylbutane. The possibility that it was 1,2-dichloro-3,3-dimethylbutane may be eliminated since both chlorine atoms were found to be rather inert (hence, primary) and since the formation of an aldehyde from the 1,2-dichloride would probably be accompanied by rearrangement of the neopentyl carbon skeleton.

Summary

1. Condensation of isobutane with allyl chloride at about $-10°$ in the presence of aluminum chloride results in a 35-40% yield of 1-chloro-3,4-dimethylpentane and a 13-15% yield of 1,2-dichloro-4,4-dimethylpentane.

2. At a higher temperature, for example $0-5°$, the product consists essentially of paraffinic hydrocarbons because of interaction of the chloroheptanes with the isobutane.

3. The principal product of the reaction of isobutane with vinyl chloride at $-10°$ in the presence of aluminum chloride is 1,1-dichloro-3,3-dimethylbutane which is obtained in 40% yield.

4. A reaction mechanism is proposed and evidence in support thereof presented.

(11) H. Brunner and E. H. Farmer, *J. Chem. Soc.*, 1044 (1937).

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[Contribution from the Chemical Laboratory, University of Rochester]

Photochemical Investigations. VI. The Photochemical Reaction between Hydrogen and Iodine Monochloride

By Lawrence J. E. Hofer[1,2] and Edwin O. Wiig

In the course of a study of the inhibiting effect of iodine monochloride on the hydrogen–chlorine photo-reaction, Rollefson and Lindquist[3] observed in a preliminary experiment that a mixture of hydrogen and iodine monochloride exposed to light of λ 4300 to 5600 Å. absorbed by iodine monochloride did not react to produce hydrogen chloride. Furthermore, a mixture of hydrogen, chlorine and iodine monochloride exposed to light absorbed by iodine monochloride only gave

no reaction whereas exposure to light absorbed by chlorine only resulted in the formation of hydrogen chloride. Mellor and Iredale,[4] however, found that 20 mm. iodine monochloride in one atmosphere of hydrogen reacted slowly in the radiation from an ordinary electric light bulb, more rapidly in diffuse daylight and very rapidly in direct sunlight. This observation was confirmed by Ashley and West[5] who observed an easily measurable reaction on exposure of pure hydrogen and iodine monochloride to the light of a mercury arc. In both these investigations the main products were identified as hydrogen chlo-
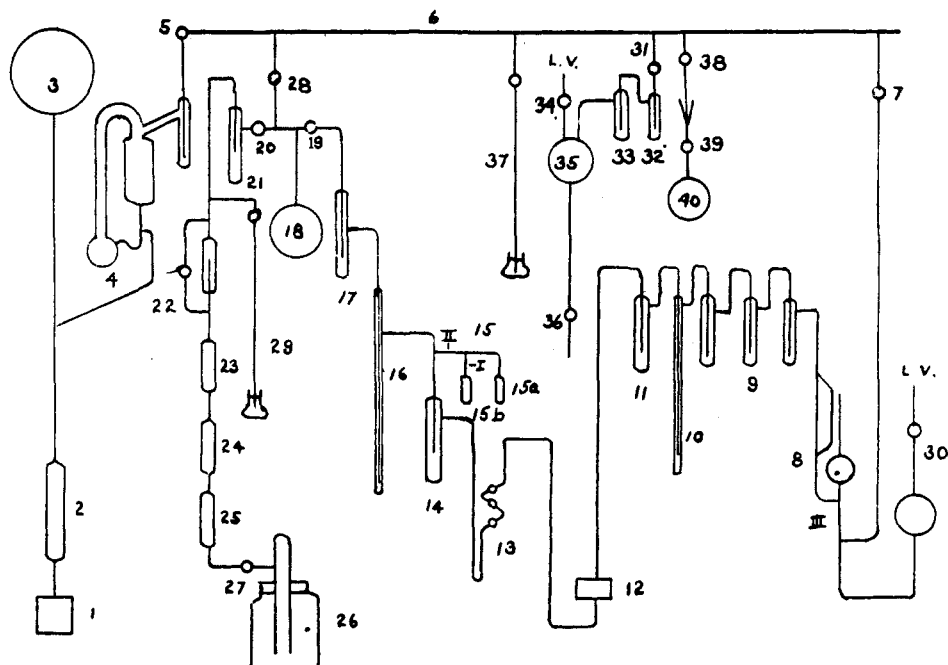
Fig. 1.—Apparatus.

ride and iodine, no appreciable amounts of hydrogen iodide being found. Ashley and West also observed that traces of impurities (stopcock grease, etc.) markedly increased the rate of the photo-reaction.

The experimental conditions were quite different in the three investigations cited. Rollefson and Lindquist, for example, used equal small pressures of hydrogen and iodine monochloride whereas Mellor and Iredale had present roughly forty times as much hydrogen as iodine monochloride. Rollefson and his co-workers[3,6] suggested that their failure to observe reaction at low hydrogen pressure was due to the removal of chlorine atoms by the reaction $Cl + ICl \rightarrow Cl_2 + I$ rather than reaction with hydrogen to produce hydrogen chloride. Since quantitative data for the photolysis of mixtures of hydrogen and iodine monochloride have apparently not been obtained, a systematic investigation of the reaction was started with a view to elucidating the mechanism.

Experimental

Materials.—The iodine monochloride, prepared and purified by the method of Cornog and Karges,[7] was sealed in place on the apparatus at 15a, Fig. 1. With the iodine monochloride cooled to $-78°$ the apparatus was evacuated by means of a mercury diffusion pump backed by an oil pump. Liquid air was placed on the bulb at 15b. After three hours evacuation with the liquid air and Dry Ice-bath in place, the Dry Ice was removed and a considerable fraction of the iodine monochloride distilled into 15b which was then sealed off at I. A middle fraction was then distilled into trap 14 cooled to $-78°$ and containing

(6) Rollefson and Potts, *J. Chem. Phys.*, **1**, 400 (1933).

(7) "Inorganic Syntheses," Vol. I. McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 165.

a small amount of analytical grade iodine. Bulb 15a was sealed off at II. The all-glass valves, 16 and 10, were then closed. These were made according to the design of Willard[8] with the modification due to Gantz and Walters in this Laboratory of a Nonex inner capillary tube.

Hydrogen was prepared by electrolysis of a 30% solution of sodium hydroxide between pure nickel electrodes, 26. The gas was passed successively over anhydrous calcium chloride, 25, platinized asbestos at 300° to remove oxygen, 24, solid sodium hydroxide to remove water, 23, and finally through a liquid air trap to remove the last traces of moisture.

Apparatus and Procedure.—A typical experiment was carried out as follows. The entire apparatus was evacuated to a sticking vacuum. Hydrogen was generated and the generator inner tube flushed four times to remove oxygen. The system was again evacuated to a sticking vacuum. Stopcock 20 was closed and the system between 27 and 20 filled with hydrogen at atmospheric pressure. With stopcocks 28 and 19 closed, stopcock 20 was opened and hydrogen allowed to leak into storage bulb 18 through the by-pass, 22. When the storage bulb was full as indicated by the manometer 29, stopcocks 5 and 7 were closed and 28 opened, filling the manifold 6 with hydrogen.

At this point the run itself began. With Dry Ice-acetone on bubbler 13, some of the iodine monochloride in 14 was distilled into 13. Liquid air was placed around the trap at 17 and stopcock 19 opened *and closed.* The all-glass stopcocks, first 16 and then 10, were opened by heating the quartz tip until the inner tube blew open. Stopcocks 7 and 30 on the McLeod gage were carefully opened simultaneously, filling the entire system with hydrogen.

Meanwhile bulb 35 had been filled with water and mercury bubbler 32 and silver nitrate solution bubbler 33 flushed with hydrogen by allowing the water to run out of the bulb through stopcock 36. The bulb, 35, was carefully refilled after the flushing operations.

A large bath of water maintained at 28.0 $\pm$ 0.1° was placed around bubbler 13, a Dry Ice-acetone bath around trap 11 and the freezing mixture then removed from around trap 14. Stopcock 28 was closed and 19 opened. Water

(8) Willard, THIS JOURNAL, **57**, 2328 (1935).

was now allowed to run slowly out of flask 35, thus pulling hydrogen through the iodine monochloride bubbler 13, the reaction cell 12, trap 11 at −78° and the McLeod gage 8. After the hydrogen had run for thirty minutes liquid air was placed around the traps at 9 and the reaction mixture illuminated at 12. Unreacted iodine monochloride and the iodine formed condensed in trap 11 while the hydrogen chloride was caught in traps 9. (The room during this period was kept at about 30° to prevent condensation of iodine monochloride in the cell.) It should be noted that the system from all-glass stopcock 16 to all-glass stopcock 10 was painted a flat black.

After illumination a Dry Ice–acetone-bath was placed around trap 14 and the hydrogen supply stopped. The hydrogen in the system was pumped out, barely perceptibly at first to ensure catching all the hydrogen chloride in the traps at 9. Any iodine monochloride in the saturator bubbler distilled into trap 11. Finally the system was evacuated down to a sticking vacuum with the mercury diffusion pump. All-glass stopcocks 16 and 10 were then closed in that order. The mercury level in the McLeod gage was raised to the level indicated by III. The liquid air was removed from the traps at 9 and one of those traps cooled with a Dry Ice–acetone mixture instead, thus evaporating the hydrogen chloride gas into the McLeod gage where its pressure was measured. The volume of the system between III and stopcock 10 (which is the volume of the hydrogen chloride produced) was determined by properly expanding a known volume of air from bulb 40.

The photolysis system, mounted on an optical bench, consisted of (a) an H3 85-watt General Electric high pressure mercury vapor lamp in a blackened brass housing, (b) two thicknesses of cobalt blue glass and 5 mm. of a 3% quinine sulfate in 3% sulfuric acid solution to isolate the 4358 Å. mercury line, (c) a quartz lens 5.5 cm. diameter and 12 cm. focal length, (d) a cylindrical Pyrex reaction cell (7.3 cm. long and 4 cm. diameter) with plane parallel windows and (e) a cylindrical quartz actinometer cell just after the reaction cell. The lamp was always allowed to run until a constant output was attained (about one and a half hours). Then the actinometer cell containing a weighed amount of standard uranyl oxalate solution was exposed behind the reaction cell with no iodine monochloride present. The actinometer solution was titrated with potassium permanganate according to the method of Leighton and Forbes[9] except that the solution was not stirred while being exposed. After the light source had been standardized in this way it was not turned off until the hydrogen–iodine monochloride photolysis had been completed. It was assumed that the light source remained constant during this period (five to six minute exposure).

Absorption of light by iodine monochloride was very carefully measured by means of a photronic cell and a microammeter. At 28° light of λ 4358 Å. was 87.4% absorbed by the reaction mixture. It should be pointed out that great care was taken to maintain the iodine monochloride saturating bubbler at 28.0 ± 0.1° in every run. The light losses through the actinometer cell and also through the reaction cell were measured in the same way. Assuming that the two windows of a given cell are identical the number of quanta absorbed by the reaction mixture is readily calculated.

Results and Discussion

The values of the quantum yield as determined in four experiments are given in Table I. Preliminary experiments with iodine monochloride which had not been as highly purified gave considerably higher values and have not been included.

To account for the observed quantum yield of 1.5 and also to explain the results of the earlier

(9) Leighton and Forbes. THIS JOURNAL, 52, 3139 (1930).

TABLE I

QUANTUM YIELD OF THE HYDROGEN-IODINE MONO-CHLORIDE REACTION

Transmission of front window of actinometer cell				0.894
Transmission of rear window of reaction cell				.896
Fraction of λ 4358 Å. absorbed by reaction mixture at 28°				.874
Volume of McLeod gage system, cc.				275

	Expt. 1	Expt. 2	Expt. 3	Expt. 4
Einstein absorbed act. × 10⁵	6.62	6.33	6.24	6.12
Time of irrad. act., hr.	8.00	10.00	10.00	10.00
Time of irrad. cell, min.	5.00	6.00	6.00	6.00
Einstein absorbed cell × 10⁷	7.54	6.91	6.82	6.68
Pressure McLeod gage, mm. × 10³	67.3	81.2	71.8	58.6
Temperature products	26°	27°	25°	26°
HCl produced, mole × 10⁷	9.9	12.0	10.6	8.66
Quantum yield	1.32	1.73	1.55	1.29
Average quantum yield		1.5		

investigations the following mechanism may be considered:

			ΔH, kcal.	$E_{act.}$, kcal. (Hirschfelder)
(1)	$ICl + h\nu \longrightarrow I + Cl$			
(2)	$Cl + H_2 \longrightarrow HCl + H$		+ 0.9	6.5
(3)	$H + ICl \longrightarrow HCl + I$		−52.2	2.7
(4)	$Cl + ICl \longrightarrow Cl_2 + I$		− 7.5	2.7
(5)	$I + I + M \longrightarrow I_2 + M$		−35.4	

If only reactions (1), (2), (3) and (5) were involved, the quantum yield would be exactly two. In the present work the quantum yield is definitely less than two. Furthermore Rollefson and Lindquist[3] found no reaction occurred when the ratio of the hydrogen to the iodine monochloride pressure is low. These facts lead one to suspect that reactions (2) and (4) compete for the chlorine atom. Whether (2) or (4) predominates will depend on the relative number of collisions which the chlorine atom will undergo with hydrogen and iodine monochloride molecules and also on the efficiency of these collisions in producing reaction. This latter is a function of the activation energy and also of the entropy of the reaction or the steric factor. All of these factors may be calculated or at least estimated.

If the collision diameters of iodine monochloride, hydrogen and the chlorine atom are taken as 3.7, 1.07 and 1.8 Å., respectively, then under the conditions of the present experiments calculations show that a chlorine atom undergoes practically nineteen times as many collisions with hydrogen, reaction (2), as with iodine monochloride, reaction (4). However, reaction (4) has a lower energy of activation than reaction (2). As determined by Rodebush and Klingelhoefer[10] reaction (2) has an energy of activation of 6.1 ± 1 kcal. while from the Hirschfelder rule the value is calculated to be 6.5 kcal. The collision efficiency as determined directly by Rodebush and Klingel

(10) Rodebush and Klingelhoefer, ibid., 55, 130 (1933)

hoefer is 3.3×10^{-5} at $25°$. The energy of activation of reaction (4) is not so easily obtained accurately. The Hirschfelder rule gives 2.7 kcal. Rollefson and Potts[6] calculated it to be 4 kcal. by a modification of Eyring's method. The latter value leads to an Arrhenius factor of 1.26×10^{-3} at $27°$. The ratio of the relative rates of the reaction of a chlorine atom with a hydrogen molecule and with an iodine monochloride molecule then becomes

$$19 \times \frac{3.3 \times 10^{-5}}{1.26 \times 10^{-3}} = \frac{1}{2}$$

Since the iodine monochloride reaction with chlorine atoms is less than half as probable as the hydrogen reaction with chlorine atoms due to the steric factor, it follows that both reactions are about equally probable under the present experimental conditions. This means that the quantum yield should be one since for every two chlorine atoms formed by photodissociation one will undergo reactions (2) and (3) forming two molecules of hydrogen chloride and the other will undergo reaction (4). This is in good agreement with the experimental quantum yield of 1.5.

On the other hand, the value of the activation energy of the iodine monochloride reaction with chlorine atoms may be the lower value obtained by the Hirschfelder rule, which leads to a reaction rate nearly one hundred times as rapid. Since traces of impurities speed up the reaction very considerably, as Ashley and West[5] point out,

there is a possibility that the observed reaction is due largely to impurities though great care was taken in the present work to use purified materials and to avoid stopcock grease. The value of 1.5 for the quantum yield might, therefore, appear to be an upper limit to the true yield.

However, if 1.5 is really the quantum yield, and the data of Ashley and West seem to support this view since they found the reaction seemed to approach a minimum, then the energy of activation of (4) must be large enough for (2) to compete successfully with (4) for the chlorine atom under conditions of high hydrogen pressure. On the other hand at low pressures, when the hydrogen pressure is roughly the same as that of the iodine monochloride, reaction (2) will proceed so slowly that practically all of the chlorine atoms will undergo reaction with iodine monochloride. Thus there is no essential conflict in the results of Rollefson and Lindquist, Mellor and Iredale, Ashley and West and the present authors.

Summary

The quantum yield of the photochemical reaction of hydrogen and iodine monochloride in a flow system was determined to be about 1.5 at an iodine monochloride pressure of 40 mm. and a hydrogen pressure of about 715 mm. A mechanism is advanced to account for the present data as well as for the results of previous investigators.

The Heat Capacity and the Entropy of Hydrated Lanthanum Magnesium Nitrate

By Frank J. Fornoff,[1] Kenneth S. Pitzer and Wendell M. Latimer

Heat capacity data over sizable temperature ranges and the corresponding entropies are available for only a few rare earth salts.[2] The present work was begun to obtain data for compounds of additional rare earths. A comparison of the thermodynamic properties of these elements will thus become possible.

Since previous studies have been made on sulfate octahydrates, it would have been desirable to use the same salt for additional elements. Lanthanum, however, does not form such a sulfate, and that of cerium is not isomorphous with those already studied.[3] After the properties of

a hundred and fifty series of rare earth salts had been reviewed, the double magnesium nitrates $2R(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$, were selected for the present work. They form an isomorphous series for at least the first eight elements of the group and are readily prepared in the form of large crystals of reproducible composition.

Experimental

Material.—The source of lanthanum was a sample of oxide kindly loaned by Prof. L. L. Quill, then at the Ohio State University, now at the Michigan State University. It had been spectrographically studied by Mr. W. H. Thomas at the Ohio State University. The principal lines of other rare earth elements were missing. The oxide was mixed with the stoichiometric quantity of Baker and Adamson c. p. basic magnesium nitrate, and both were dissolved in c. p. nitric acid. After filtration the solution was evaporated to crystallization. The salt was recrystallized from water a number of times. Soluble impurities such as nitric acid and magnesium nitrate were further removed by several fractional crystallizations. The amount of water in the sample was adjusted by placing the sample in a desiccator with a weak desiccant for a short time.

The average residue on igniting samples was 29.35% while the theoretical is 29.25%. The ratio of lanthanum

(1) National Research Fellow in Chemistry, 1939–1940; present address: Lehigh University, Bethlehem, Pennsylvania.

(2) (a) $Sa_2(SO_4)_3 \cdot 8H_2O$ from 17 to 300° A., Ahlberg and Freed, This Journal, **57**, 431 (1935); (b) $Gd_2(SO_4)_3 \cdot 8H_2O$ from 16 to 300° A., Ahlberg and Clark, *ibid.*, **57**, 437 (1935); (c) $Eu_2(SO_4)_3 \cdot 8H_2O$ from 60 to 300° A., Long and Degraff, *ibid.*, **64**, 1346 (1942); (d) studies over limited ranges have been reported by Clark and Keesom, *Physica*, **2**, 1075 (1935); Giauque and MacDougall, *Phys. Rev.*, **44**, 235 (1933); and Giauque, Stout, Egan and Clark, This Journal, **63**, 405 (1941).

(3) Spencer, "The Metals of the Rare Earths," Longmans, Green and Co., London, 1919, pp. 81, 101.