that in these experiments the minimum average rate of steam flow over the sample was 32 cm. per second, as compared to Mayers' maximum flow of 30 cm. per second. The actual rates of gasification compare with those of Mayers as shown below.

RATE OF GASIFICATION IN MOLES × 10^{-6}/SQ. CM. SEC.

Temp., °C.	Warner (electrode carbon)[a]	Mayers (monolithic graphite)
850	0.18	0.09
900	1.8	0.22

[a] National Projector Carbon, National Carbon Co., Cleveland, Ohio.

Admitting the validity of these saturation pressures, there remain the problems of the activation energies and an explanation of why these pressures decrease with increase of temperature as was found in the treatment of the Brewer and Reyerson data (although not corroborated in the limited temperature range studied in the present experiments). The type of adsorption involved is most likely activated adsorption, so that the rate of adsorption should increase with temperature. Since it appears from the results that the adsorption equilibrum for those areas participating in the reaction is set up very rapidly there is no apparent reason for decrease in saturation pressure. It should be emphasized that in this case the adsorbing medium, carbon, is also participating in the reaction. Surface changes are continually taking place, and only the gross rate of reaction is measured. Certain areas may indeed lose activity due to a phenomenon similar to sintering of catalysts at high temperatures. At the higher temperatures the active areas which adsorb and react rapidly contribute most strongly to the gasification, while other less active areas may adsorb more slowly, and what appears to be a decrease in saturation pressure will necessarily follow. Because reaction is taking place, it is possible for unreactive areas to become active and *vice versa*.

No attempt has been made to calculate activation energies from these data since the unknowns involved preclude any such attempt. The true activation energy of this reaction may be very close to that obtained by Meyer and Sihvonen,[9] since in their experiments at very high temperatures (*circa* 2000° and 10^{-2}–10^{-4} min.) and low pressures, equal areas with low heats of adsorption would be participating in the reaction.

Acknowledgment.—The author wishes to express his appreciation to W. H. Tomlinson and Carl H. Noble for their aid in making the measurements, and to Dr. G. von Elbe with whom the author consulted during the course of the work.

Summary

New experimental proof has been obtained for the existence of isotherms and saturation pressures in the reaction between steam and carbon. These isotherms are of the form similar to the adsorption of a monomolecular layer of a gas on a solid adsorbent.

[9] Meyer, *Trans. Faraday Soc.*, **34**, 1056 (1938); Sihvonen, *ibid.*, **34**, 1062 (1938).

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Hydrogen Chloride as a Condensing Agent

BY J. H. SIMONS AND HAROLD HART

The use of hydrogen fluoride as a condensing agent has been demonstrated in this Laboratory,[1] and a study of the mechanism of the hydrogen fluoride catalyzed reaction between toluene and *t*-butyl chloride has been reported by Sprauer and Simons.[2] They have proposed an hypothetical mechanism which might be called a mutual acid–base catalysis[3] and have suggested that a similar mechanism might hold for other hydrogen fluoride catalyzed condensations.

Since the acidic and basic species involved in their mechanism are not ascribed to any specific chemical compound, it seemed logical that acids other than hydrogen fluoride might supply the acidic species. It was the purpose of this research to determine whether hydrogen chloride, under appropriate conditions, would have a catalytic activity similar to that of hydrogen fluoride.

The alkylation of the aromatic nucleus with certain alkyl halides and olefins and the acylation of the aromatic nucleus with an acyl halide have been accomplished successfully with the use of hydrogen chloride as the condensing agent. The reactions were carried out at temperatures varying from 75–235°, with initial hydrogen chloride pressures of 100–400 pounds per square inch. The yields in most cases were very good, with little or no tarry residues being formed. The reactions were homogeneous, which obviated the necessity of shaking.

[1] J. H. Simons, *The Petroleum Refiner*, **22**, 83 and 189 (1943).

[2] J. W. Sprauer and J. H. Simons, THIS JOURNAL, **64**, 648 (1942).

[3] As the terms acid–base or acid–base catalysis have been used in the titles of articles published since our prior publication, for example, W. F. Luder and S. Zuffanti, *ibid.*, **66**, 524 (1944), and H. C. Brown. *et al.*, *ibid.*, **66**, 431 and 435 (1944), it is probably desirable to refer to the phenomenon which we have under discussion as the "Amphoteric Medium Effect."

Materials.—The hydrogen chloride used throughout the experiments was the commercial grade supplied in steel cylinders. The benzene and toluene were ordinary stock material which had been fractionated, heart cuts with constant boiling point and refractive indices being used. Eastman Kodak Co. phenol was distilled and the material boiling 179–182° was employed. Tertiary butyl chloride, tertiary amyl chloride, isopropyl chloride and normal butyl chloride were prepared according to the methods described in "Organic Syntheses,"[4] with slight modifications. Ordinary stock acetyl chloride and benzoyl chloride were used without further purification. Eastman Kodak Co. cyclohexene was used without further purification.

Apparatus.—All of the experiments which are described below were carried out in copper bombs of approximately 520-ml. capacity. The bombs were connected by means of a brass compression fitting to a five-inch length of 1/4 inch o. d. copper tubing. The end of this was inserted into a six-inch length of 1/2 inch o. d. copper tubing and silver soldered to it by pinching the end of the latter tight around the smaller tubing. A six-inch length of 1/4 inch iron pipe was attached to the other end of the 1/2 inch copper tubing by means of a silver-soldered butt joint. The pipe was connected to a 1/4 inch forged steel tee, one end of which led to a 3000 pound per square inch stainless steel pressure gage and the other, by means of a short nipple, to a 1/4 inch forged steel globe valve. The other side of the valve was connected, by means of another short nipple, to the male part of a 1/4 inch forged steel union. The hydrogen chloride cylinder was fitted, through a drilled and tapped brass block, to a four-inch 1/4 inch iron nipple, at the end of which was the female half of a 1/4 inch forged steel union.

A glass water condenser, nine inches in length, surrounded the 1/2 inch copper tubing and extended three inches above the butt joint. It was attached by means of rubber stoppers, and water was kept running through the condenser during the course of the reaction. This condenser prevented any reactant liquid from coming into contact with the iron or steel parts of the apparatus.

The bombs were heated by means of an electrically heated tubular furnace, and the recorded temperatures were determined by placing a 360° thermometer within a copper well inside the furnace. At the end of the experiments the hydrogen chloride pressure was released through a train of traps and water bubblers.

Procedure.—In general, a standard procedure was followed in carrying out most of the reactions, with necessary modifications when required by the particular case at hand. The desired quantities of reactants were weighed into a beaker and poured into the bomb. The bomb was then attached to the rest of the apparatus, and water was started through the condenser. The hydrogen chloride cylinder was connected by means of the 1/4 inch forged steel union, and hydrogen chloride was admitted until the full cylinder pressure was reached. This was usually about 650 pounds per square inch. The valve on the apparatus was then closed, and the hydrogen chloride cylinder detached by opening the union. The bomb was then shaken a few times by hand to dissolve some of the hydrogen chloride vapors in the reactants. This usually decreased the pressure to approximately 200 pounds per square inch. The bomb became warm due to the heat of the solution of the hydrogen chloride. The bomb was then placed in the furnace which had been preheated at the desired temperature for twenty-four hours. It was allowed to remain there for the desired length of time, then removed and cooled until it reached room temperature. The hydrogen chloride pressure was then released through the train of bubblers, the bomb detached from the rest of the apparatus and the contents poured into a beaker and weighed.

In most cases, the hydrogen chloride dissolved in the product was removed by washing with 10% sodium bicarbonate solution followed by several washings with water. The product was dried over calcium chloride and fractionated in a small glass-packed column of approximately 8–10 theoretical plates.

Results.—The experimental conditions and results of a number of representative experiments are summarized in Table I, and the properties of the compounds prepared, together with a comparison with the literature values, are listed in Table II.

TABLE I

Alkyl or acyl compound	Moles used	Moles of arom.^{e}	Initial HCl press.	Time in hr.	Temp., °C.	Yield, %	
						Mono	Di
t-C_4H_9Cl	0.33	0.97-T	200	12	235	88	..
iso-C_3H_7Cl	.33	1.0 -T	300	6	235	67	16
n-C_4H_9Cl	.67	1.0- T	300	24	235	15	66^a
t-C_4H_9Cl	.66	2.04-B	100	12	150	45.5	24
iso-C_3H_7Cl	.7	1.98-B	100	16	235	48	44
n-C_4H_9Cl	.67	2.0 -B	100	12	195	30	60
Cyclohexene	.5	2.0 -B	250	25	208	37	27^b
C_6H_5COCl	.5	1.5 -B	250	20	200	4.4	88^c
t-C_4H_9Cl	.4	2.0 -P	400	12	75	90	..
t-C_4H_9Cl	.2	1.0 -P	...	1.5	70–150	67	..
t-$C_5H_{11}Cl$	.5	1.0 -P	...	2.5	90–160	72	..
Cyclohexene	.56	1.5 -I	250	19.5	200–220	^{d}	

[a] Per cent. recovery of unreacted n-butyl chloride. [b] Per cent. yield of cyclohexyl chloride. [c] Per cent. recovery of benzoyl chloride as benzoic acid. [d] Products were 4% recovered cyclohexene, 40% polymer, 30% cyclohexyl chloride, and 4% of a saturated hydrocarbon boiling at 195–200°. [e] T, Toluene; B, benzene; P, phenol; I, isopentane.

Discussion.—The orientation of the alkylation as catalyzed by hydrogen chloride seems to be similar to that of the hydrogen fluoride catalyzed reactions. It has been pointed out that the alkylation of toluene with tertiary butyl chloride, isopropyl chloride and normal butyl chloride in the presence of aluminum chloride takes place in both the meta and para positions (approximately 65–70% meta and 30–35% para).[5] In corresponding reactions with hydrogen fluoride, however, only the para isomer was formed[6] and this is also the case with hydrogen chloride. The monoalkyl products of the alkylations of toluene were all shown to be the para isomers, as were the dialkyl products of the alkylations of benzene.

As in the case of both hydrogen fluoride and the metallic halide catalyzed condensations of alkyl halides with benzene or toluene, yields decrease as one proceeds from tertiary to primary halides. However, in the case of the latter, a large amount of the unreacted normal butyl chloride was recovered in addition to the alkylated aromatic, so that the yields listed in Table I are actually per cent. conversion in these cases.

In the reaction of benzene with cyclohexene, two other reactions compete with the alkylation: addition of hydrogen chloride to the double bond and polymerization of the olefin. Both of these occurred, but a 37% yield of cyclohexylbenzene was obtained. The first side reaction accounted for 27% of the cyclohexene and some polymer was obtained, although not in large quantities. It

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(4) "Organic Syntheses," Coll. Vol. I, ed. 2, John Wiley and Sons Inc., New York, N. Y., 1941, pp. 142–144.

(5) J. B. Shoesmith and J. F. McGechen, *J. Chem. Soc.*, 2231–2236 (1930).

(6) J. H. Simons and S. Archer, THIS JOURNAL, **60**, 2953 (1938).

TABLE II

The first lines under each compound represent the values obtained in this research, whereas the second lines give the corresponding literature values for the same properties.

Compound	Source	B. p., °C.	$n^{20}D$	M. p. of derivative, °C.
p-*t*-Butyltoluene	*t*-Butyl chloride and toluene	188–189	1.4930	164.5–165.0[a]
		188–189	1.4929	164
p-Isopropyltoluene	Isopropyl chloride and toluene	175–176	1.4950	176–177[b]
				139.5–140.5[c]
		175.0	1.4933	176–178; 140
XX′-Diisopropyltoluene	Isopropyl chloride and toluene	216–220	1.4960	
p-*s*-Butyltoluene	*n*-Butyl chloride and toluene	193–194	1.4931	
		193.0	1.4930	
t-Butylbenzene	*t*-Butyl chloride and benzene	168.0–168.8	1.4924	169–170[d]
		167.0	1.4926	170
p-Di-*t*-butylbenzene	*t*-Butyl chloride and benzene	76–77[e]		189–190[f]
		76		190
Isopropylbenzene	Isopropyl chloride and benzene	151–152	1.4910	104–105[d]
		152.3	1.4916	106
p-Di-isopropylbenzene	Isopropyl chloride and benzene	206–207	1.4897	139.5–140.5[c]
		205.5–206.5	1.4912	140
s-Butylbenzene	*n*-Butyl chloride and benzene	172–173	1.4900	123.8–124.0[d]
		171.0	1.4902	126
Cyclohexylbenzene	Cyclohexene and benzene	236–238	1.5258	129–130[d]
		236.6–236.8	1.5254	130–131
Cyclohexyl chloride	Cyclohexene and benzene	140.0–141.5	1.4630	146.5–147.0[g]
		142–143	1.4626	146
Benzophenone	Benzoyl chloride and benzene	47.5–48.0[e]		140–141[h]
		49		141–142.5

[a] *p*-*t*-Butyl benzoic acid. [b] *p*-Toluic acid. [c] Dimethyl terephthalate. [d] Acetamino derivative. [e] Read as melting point instead of boiling point. [f] 2,6-Dinitro-1,4-di-*t*-butylbenzene. [g] Anilide of cyclohexanecarboxylic acid. [h] Benzophenone-oxime.

seems probable that alkylation of the benzene nucleus with other olefins is also possible with the use of hydrogen chloride. The alkylation of the isoparaffin, isopentane, by an olefin was shown to be accomplished to a limited extent with cyclohexene despite the competing reactions of polymerization of the olefin and the addition of hydrogen chloride to it.

A disproportionation reaction of the type

$$t\text{-}C_4H_9C_6H_5 + C_6H_5OH \longrightarrow C_6H_6 + t\text{-}C_4H_9C_6H_4OH$$

was attempted, but none of the desired products were obtained. This reaction proceeds to a small extent with hydrogen fluoride.[7]

The acylation of benzene with acetyl chloride and benzoyl chloride was attempted, using approximately the same conditions as with the alkylations, and although no acetophenone was isolated, a 4.4% yield of benzophenone was obtained. Eighty-eight per cent. of the benzoyl chloride was recovered as benzoic acid.

Reactions with Phenol.—The first reaction which was studied using hydrogen chloride as a condensing agent was the alkylation of phenol with *t*-butyl chloride. At 75° for twelve hours, a yield of 90% of *p*-*t*-butylphenol was obtained. In order to determine whether or not the hydrogen chloride actually was acting as a catalyst, the reaction was repeated under similar conditions using nitrogen as the source of pressure. Again, a very good yield of the alkyl phenol was obtained.

Since the reaction takes place in the liquid phase, it did not seem likely that pressure should have any marked effect. Therefore, the reaction was performed simply by refluxing phenol and *t*-butyl chloride for one and one-half hours, without any added catalyst, and a 67% yield of *p*-*t*-butylphenol was obtained. The probable reason for the lower yield in this case was the loss of volatile *t*-butyl chloride with the hydrogen chloride fumes through the condenser.

It has been shown by Bennett and Reynolds that when active alcohols such as *t*-butyl alcohol, triphenylcarbinol, benzyl alcohol and *p*-chloro and *p*-bromobenzyl alcohols are refluxed with phenol and hydrobromic acid, the alkylated phenol is obtained.[8] They also showed that *t*-butyl bromide and triphenylmethyl bromide condense rapidly with phenol. It is interesting that Perkins, Dietzler and Lundquist have obtained a patent for the alkylation of phenol with *t*-butyl chloride in the presence of aluminum chloride or ferric chloride at a temperature of 50–200°.[9] Obviously the reaction will take place at these temperatures whether the metallic halide is present or not. Another patent covers the tempera-

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(7) J. H. Simons, S. Archer and D. I. Randall, THIS JOURNAL, **62**, 485 (1940).

(8) G. M. Bennett and F. M. Reynolds, *J. Chem. Soc.*, 131 (1935).

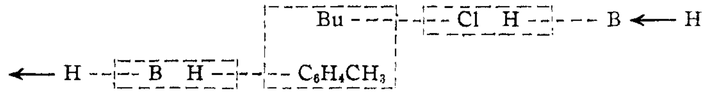
(9) R. P. Perkins, A. J. Dietzler and J. T. Lundquist, U. S. P. 1,972,599 (*C. A.*, **28**, 6532 (1934)).

ture range 20–50°.[10] It is true, however, that certain catalysts such as aluminum chloride, hydrogen fluoride[11] and zinc chloride[8] will catalyze the reaction at temperatures at which it will not occur rapidly without an added catalyst.

Tertiary amyl chloride has also been condensed with phenol by refluxing for two and one-half hours without any added catalyst, to give a 72% yield of *p*-*t*-amylphenol.

Proof of Hydrogen Chloride Catalysis.—To actually demonstrate the catalytic activity of hydrogen chloride *t*-butyl chloride and toluene were heated at 235° for twenty-two hours, under a nitrogen pressure of approximately 575 pounds per square inch. At the end of this time, the contents of the bomb were treated in the usual manner and fractionated. Approximately 84% of the toluene and 55% of the *t*-butyl chloride were recovered unchanged, and a small quantity (approximately 10% of the theoretical) of higher boiling material (probably *t*-butyltoluene) was isolated. This is certainly not comparable to the 88% yield of *p*-*t*-butyltoluene obtained by use of hydrogen chloride as the catalyst. It can also be argued that due to prolonged heating at 235°, *t*-butyl chloride may have decomposed to give a small quantity of hydrogen chloride which was sufficient to catalyze the alkylation to some extent, but because of the dilution with nitrogen, could not be formed in sufficient quantity to give a good yield of the alkyl toluene.

Mechanism.—As this work followed from the kinetic study of the hydrogen fluoride catalyzed condensation of *t*-butyl chloride and toluene and as a similarity between the activity of hydrogen chloride and hydrogen fluoride as condensing agents has been found, a mechanism for these condensations, similar to that already proposed for hydrogen fluoride condensations, may be offered. Using the same reaction, which has been shown to give good yields of *p*-*t*-butyltoluene, the mechanism might be formulated as



The possibility of other substances, such as traces of water, supplying the basic species is quite strong. Although this mechanism is suggested without definite experimental proof, it seems to be at least subject to consideration.

Summary

1. The activity of hydrogen chloride as a condensing agent has been demonstrated. The alkylation of benzene and toluene has been accomplished using alkyl halides and olefins, and the acylation of benzene with an acyl halide has been accomplished, using hydrogen chloride as the condensing agent. The alkylation of an isoparaffin is also indicated.
2. Although the reactions are not as readily executed as those which use hydrogen fluoride or aluminum chloride as the catalyst, because of the pressure equipment required, the yields are good and the reactions take place without the formation of tarry residues.
3. Hydrogen chloride resembles hydrogen fluoride more than it does the metallic halides in its catalytic activity.
4. Phenol can be alkylated directly with active tertiary alkyl halides, without any added catalyst.

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[10] M. E. Putnam, E. C. Britton and R. P. Perkins, U. S. P. 2,039,344 (*C. A.*, **30**, 4176 (1936)).

[11] J. H. Simons, S. Archer and H. J. Passino, THIS JOURNAL, **60**, 2957 (1938).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BANTING INSTITUTE, UNIVERSITY OF TORONTO]

Carbohydrate C-Nitroalcohols: 1-Nitro-1-desoxy-D-mannitol

BY JOHN C. SOWDEN AND HERMANN O. L. FISCHER

Due to the present availability of the nitroparaffins, the reaction of these compounds with various types of aldehydes to produce nitroalcohols has received much attention in recent years.[1] Successful application of this reaction to the aldose sugars would produce carbohydrate C-nitroalcohols containing the grouping —C—NO_2, an interesting new type of derivative, differing from the well-known sugar nitrates containing the grouping —C—O—NO_2.

Apparently, the only recorded application of thenitro paraffin–aldehyde condensation reaction to the sugar series consists of the experiments described by Pictet and Barbier.[2] These authors treated glycolaldehyde, glyceraldehyde, L-arabinose and D-glucose with nitromethane and alkali but made no attempt to isolate the expected C-nitroalcohols. Their reaction mixtures were reduced and then treated with nitrous acid in an attempt to prepare the sugar alcohols containing one more carbon atom than the original sugars. However, no product could be identified from glyceraldehyde or L-arabinose, and the product isolated in low yield, from D-glucose, reported to be α-glucoheptitol, did not agree in every particu-

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[1] Excellent reviews on the chemistry of the nitroparaffins have recently appeared by Hass and Riley, *Chem. Rev.*, **32**, 373 (1943), and by Hass, *Ind. Eng. Chem.*, **35**, 1146 (1943).

[2] Pictet and Barbier, *Helv. Chim. Acta*, **4**, 924 (1921).