Summary

Based on the rotational data, the velocity constant of the hydrolysis of α-ethylthioglucofuranoside in 0.01 N hydrochloric acid at 100° was found by Green and Pacsu to be $K \times 10^5 = 6250$. It has now been shown that the change in rotation does not go parallel with the actual progress of the hydrolysis. Quantitative estimation of the glucose formed during the reaction indicates that only 9.5% of the thioglucofuranoside is hydrolyzed when the drop in rotation shows an 85% completion of the hydrolysis.

Working up the solutions after twenty-five minutes and three hours of hydrolysis, two new thioglycosides, β-ethylthioglucofuranoside and α-ethylthioglucopyranoside, respectively, have been isolated. From the latter compound a crystalline tetraacetate has been prepared. A possible mechanism is suggested for this unprecedented hydrolysis, in which about one-half of the α-ethylthioglucofuranoside changes into glucose and mercaptan whereas the other half escapes the hydrolyzing effect of the acid by shifting the furanoid ring into the acid resistant pyranoid ring.

Solvent Effects in Addition Reactions. I. Addition of Hydrogen Bromide and Chloride to Cyclohexene and 3-Hexene

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Introduction

In many additions to unsaturated carbon compounds it is commonly believed that an electron-seeking reagent (A) accepts a pair of electrons from one of the unsaturated carbon atoms while a nucleus-seeking reagent (D) donates a pair of electrons to the other unsaturated carbon atom. The two addenda apparently may exist as separate molecules, ions or fragments or originally may be united in the same molecule.

$$\text{>C}::\text{C<} + \text{A}:\text{D} \longrightarrow -\overset{|}{\underset{|}{\text{C}}}:\overset{|}{\underset{|}{\text{C}}}-$$
$$\underset{\text{A}}{\downarrow}\ \underset{\text{D}}{\uparrow}$$
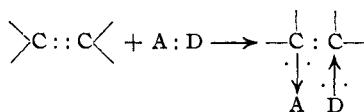
Opinions differ as to the order of these steps. Ingold[1] cited evidence to show that the electron-seeking or positive addendum is attached first and a similar mechanism has been employed by Whitmore[2] to explain the rearrangement of intermediate positive organic fragments. On the other hand, Ogg[3] advanced the theory that addition of the nucleus-seeking or negative addendum is the first step.

Regardless of which addendum is attached first, or if both are attached simultaneously, it is reasonably evident that the presence of a strong electron-seeking addendum is essential to the occurrence of many addition reactions. Proof of this lies in the fact that all substances which add spontaneously to unsaturated carbon compounds appear to be electron-seeking reagents, as Ingold has pointed out, and in the further fact that all catalysts for these addition reactions, such as strong acids, halides of boron and aluminum, etc., seem to fall within the same category. If this is a true picture, it follows that the presence of any substance, such as a solvent, which tends to combine with the electron-seeking reagent, and thus reduce its effectiveness, should retard or prevent addition. This should be particularly true of substances containing electron-donor atoms, such as oxygen and nitrogen.

To test this hypothesis, we have studied the addition of hydrogen bromide and hydrogen chloride to two olefins in various solvents. The reactions were carried out in dilute homogeneous solution and relative rates determined. In order to avoid directional influences and the formation of isomers, cyclohexene and 3-hexene only were employed. The results of these studies are given in Tables I–IV. The initial hydrogen halide concentrations are given in normality. It is evident that the reactions are remarkably rapid in non-donor solvents, such as xylene and heptane, and extremely slow in strong donor solvents, like ether and dioxane.

(1) Ingold, Chem. Rev., 15, 268–272 (1934).
(2) Whitmore, "Organic Chemistry," D. Van Nostrand Co., New York, 1937, pp. 665, 670–672.
(3) Ogg, This Journal, 57, 2727 (1935).

TABLE I
REACTION OF CYCLOHEXENE WITH HYDROGEN BROMIDE IN VARIOUS SOLVENTS

Time in min.	Solvent: Di-oxane 0.195 (2.7:1)	Ether-benz.a 0.253 (2.1:1)	Ether 0.118 (1:1)	Ether 0.118 (5:1)	Ether 0.118 (10:1)	Chloro-form 0.218 (2.4:1)	Nitro-benz. 0.208 (2.6:1)	Ether-xyleneb 0.115 (1:1)	Ether-xyleneb 0.115 (5:1)	Xylene 0.131 (1:1)	Xylene 0.131 (5:1)
2			0.00	0.68	4.16			59.21	62.18	81.42	84.09
4			.94	1.02	7.73			63.14	65.24	85.73	86.24
5	11.53	9.93				27.15					
6			2.12	3.65	8.92		30.56	67.25	69.34	86.24	87.76
8			3.30	3.65	11.31			70.30	72.31	87.31	88.84
10	13.82	10.52	4.50	4.76	12.50	38.17	39.25	72.31	74.32	87.76	89.37
20		10.93				50.24	51.02				
30		12.38			20.15	57.38	56.94		77.38		92.05
40	19.73	12.71				61.06	61.55				
50		15.04		16.07	26.10	65.48		77.38	80.43	92.05	93.12
60	21.56	15.78				67.72	69.64				
70				19.55	30.86			78.42		93.12	94.18
80	22.93	18.79				71.35	73.74				
90			15.73	24.91	38.52			79.47	82.44	94.18	

a 40% ether, 60% benzene, by volume.   b 10% ether, 90% xylene, by volume.

TABLE II
REACTION OF 3-HEXENE WITH HYDROGEN CHLORIDE IN VARIOUS SOLVENTS

Time in min.	Solvent: Ether 0.131 (5:1)	Ether 0.131 (10:1)	Di-oxane 0.140 (1:1)	Nitro-benz. 0.144 (1:1)	Butyl brom. 0.123 (1:1)	Hep-tane 0.128 (1:1)	Xylene 0.117 (1:1)	Xylene 0.117 (5:1)	Xylene 0.117 (10:1)
2	0.08	0.10	0.00	23.67	32.02	58.76		37.36	
4	.12	.16		26.12	32.41	59.47	35.40		
5								42.29	44.34
6	.18	.22	.72		33.80	66.95	38.38		
8	.22	.28		29.04	34.25	69.21	39.40		
10	.24	.30		30.15	35.10	72.87	40.34		
30	.58	.74	.72	31.82	37.80	76.00			57.19
90	1.52	1.95	1.43	43.10	44.50	87.37	58.21	60.17	70.04

TABLE III
REACTION OF CYCLOHEXENE WITH HYDROGEN CHLORIDE IN VARIOUS SOLVENTS

Time in min.	Solvent: Ether 0.132 (10:1)	Ether 0.132 (20:1)	Ether 0.132 (30:1)	Di-oxane 0.140 (1:1)	Nitro-benz. 0.144 (1:1)	Heptane 0.128 (1:1)
2		0.70	0.85	0.00	23.67	54.78
4		.85	1.02	.00	25.34	57.04
6		.88	1.08	.00	26.53	58.44
8		.89	1.10	.00	27.78	60.23
10		.90	1.12	.00	28.13	63.34
30						69.72
90	0.00	1.55	2.10	.72	37.46	77.90

TABLE IV
REACTION OF 3-HEXENE WITH HYDROGEN BROMIDE IN BENZENE: 0.114 N HBr; 1:1 RATIO

Time, min.	% HBr reacted
10	93.9
20	95.4
40	96.4
70	97.9
175	99.0

The extreme rapidity of these reactions in non-donor solvents is indicated also by the pronounced temperature rise observed when the olefin and hydrogen halide are mixed in such solvents. The data are given in Table V.

TABLE V
TEMPERATURE RISE FOR HYDROGEN BROMIDE ADDITION IN HYDROCARBON SOLVENTS

A — 0.206 N HBr in xylene with 1.02 equivalents of 3-hexene		B — 0.194 N HBr in heptane with 1.02 equivalents of cyclohexene	
Time, sec.	T, °C.	Time, sec.	T, °C.
0	25.5	0	23.3
45	30.7	45	30.6
75	32.0	75	31.4
105	32.4	105	32.0
135	32.6	135	32.4
165	32.8	165	32.6
195	32.9	195	32.8

It is significant that the reaction rates appear to depend on the electron–donor activity of the

solvent rather than upon its dielectric constant. For example, the reactions cited are rapid in anhydrous benzene (D, 2.27) and slow in dioxane (D, 2.10).

Experimental

Olefins.—Cyclohexene was from Eastman Kodak Co. and 3-hexene from the Jackson Laboratory of the du Pont Co. Both compounds were fractionated carefully and only middle portions used.

Solvents.—The hydrocarbons, ether and dioxane were refluxed over sodium shavings. Chloroform, nitrobenzene, etc., were dried over anhydrous calcium chloride. All solvents were distilled several times after drying and only middle portions retained.

Hydrogen Halides.—Hydrogen bromide was obtained by the action of bromine on naphthalene. The gas was passed through four towers of naphthalene, one of calcium chloride, and one of phosphorus pentoxide on glass wool. Hydrogen chloride was prepared by the action of sulfuric acid on sodium chloride and hydrochloric acid and dried by bubbling through sulfuric acid and passage over calcium chloride.

Procedure.—Hydrogen halide was bubbled through dry, freshly distilled solvent until the increase in weight indicated a normality between 0.2 and 0.3. A 10-ml. sample was withdrawn, added to excess standard sodium hydroxide, thoroughly agitated and back-titrated with standard hydrochloric acid, using methyl orange as the indicator. A 50-ml. sample of stock solution was then withdrawn, placed in a glass-stoppered Erlenmeyer flask, and the latter suspended in a constant temperature bath maintained at 25°. The proper amount of freshly distilled olefin was then measured out volumetrically and diluted with solvent to 50 ml. This solution was adjusted to 25°, added quickly to the hydrogen halide solution and the flask stoppered and returned to the constant temperature bath. Samples were withdrawn periodically for analysis by titration. In some cases, 0.1 to 0.15 N solutions were prepared, analyzed and the desired amount of undiluted olefin added to a 100-ml. sample of the halide solution.

Temperature Rise.—The rise in temperature during the initial period of the addition of hydrogen bromide in hydrocarbon solvents was observed as follows. A slight excess of pure olefin was added rapidly from a pipet to 250 ml. of analyzed hydrogen bromide solution contained in a 500-ml. Dewar flask. The flask was stoppered tightly, agitated, and the rise in temperature noted at fifteen-second intervals by means of a thermometer graduated in tenths.

Accuracy.—During the experiments small quantities of hydrogen halides were lost by volatilization, particularly from the hydrocarbon solvents and, to a lesser extent, from nitrobenzene, chloroform, and butyl bromide. Losses from ether and dioxane were not noted. Losses of hydrogen chloride were greater than those of hydrogen bromide. However, many blank determinations, carried out under identical conditions, showed that in the extreme cases the loss of hydrogen bromide was under 5% of the total in solution, while the loss of hydrogen chloride was under 10%. In most of the reported work the probable errors through this effect are very much less than these figures. Losses occurred only when the solutions were in contact with air, as when the flasks were opened, or when the solutions were pipetted. The experiments were found to be quite reproducible.

Traces of peroxides are known to increase the velocity of hydrogen bromide additions in some cases. In order to obviate catalysis of this type as much as possible only freshly distilled materials were used. It should be pointed out that solutions in ether and dioxane might well present the most favorable conditions for peroxide formation, both from the solvent and from the olefin. On the other hand benzene and xylene do not appear to form peroxides and in these media the addition reactions are so rapid as to allow little time for the formation of olefin peroxides. The data are thus directly opposite to those which would be expected if peroxides were important in increasing the velocity of hydrogen bromide addition.

Because of the extremely rapid addition of hydrogen bromide in the hydrocarbon solvents as well as the rapid temperature rise observed for these cases, it does not appear possible to follow the reaction rates with sufficient accuracy to warrant derivation of rate expressions. Preliminary calculations of this kind failed to reveal satisfactory conclusions. For this reason further investigations of similar addition reactions are in progress. It appears now that hydrohalogen and halogen additions to olefins do not follow simple second order rate equations though further data are needed to establish the mechanism.

Summary

In the addition of hydrogen bromide and hydrogen chloride to two typical olefins, it has been shown that the rate of reaction decreases with the increasing tendency of the hydrogen halide to coordinate with a donor atom from the solvent.