The Action of Halosulfonic Acids on (+)3-Methylhexane

BY ROBERT L. BURWELL, JR., LUCIEN G. MAURY AND ROBERT B. SCOTT

In contrast to the case of sulfuric acid at 60°, agitation of (+)3-methylhexane with chloro- or fluorosulfonic acid at −78° or −33° results in rates of loss of rotation considerably in excess of those of isomerization to 2-methylhexane. Similar, though smaller, excess is observed with chlorosulfonic acid–sulfuric acid mixtures at 0° and still smaller excess with sulfuric acid at 0° and 30°. In further contrast to the case with sulfuric acid at 60°, with halosulfonic acids at low temperatures, the ratio of rate constants of loss of rotation and of isomerization depends upon the degree of stirring. The mechanism seems similar to that proposed for sulfuric acid, but the rate of isomerization of the chain propagating species (carbonium ions), which has just about attained equality with the rate of hydride ion transfer at 60°, falls below that of hydride ion transfer to an increasing degree as the temperature is lowered.

At −78°, (+)3-methylheptane is relatively rapidly racemized by agitation with chlorosulfonic acid-d, but there is very little accompanying isomerization or isotopic exchange,[1] whereas with 96% sulfuric acid at 60°, the three reactions have rates of the same order of magnitude. To accompany a more detailed study of the sulfuric acid case,[2] study of the behavior of (+)3-methylhexane with chlorosulfonic acid was undertaken.

Experimental

Materials.—Preparation of the hydrocarbons has been described.[2] The chlorosulfonic acid employed was of two sources: (a) freshly distilled commercial material, (b) synthetic material prepared as follows[3]: Phosphorus pentachloride (150 g.) was added slowly to fuming sulfuric acid (10.2% SO₃) (200 g.) at 15°. After standing 12 hours at 25° the material was distilled in all glass Vigreux column of perhaps three theoretical plates. The fraction boiling at 52° was accepted. The column had to be clean and devoid of greased joints, since reduction products of the acid apparently catalyze its decomposition.

Acid prepared by (a) from Eastman Kodak Co. Practical Grade was pale yellow. Exposure to air for a few minutes or standing in a closed bottle for a few days caused it to become orange-yellow. The synthetic material was colorless and darkened on standing more slowly than the commercial product.

The commercial acid contained an impurity which catalyzed the reaction

$$2HClSO_3 = H_2SO_4 + SO_2Cl_2$$
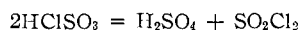
since upon attempting to fractionate the acid in a column packed with glass helices, we obtained an excellent yield of sulfuryl chloride.

Fluorosulfonic acid (General Chemical Company) was fractionated in the small distilling column. It became colored much more slowly than the chlorosulfonic acid.

Procedure.—Halosulfonic acids and alkanes form a heterogeneous system. The reaction mixture was stirred by a magnetic stirrer in two ways, *rapid* and *standard*.[2] The former produced a better "emulsion" and is taken as giving better stirring. The reactants were used in the ratio of 3.25 cc. of hydrocarbon to 4.50 cc. of acid.

Thermostating at −78° was by a Dry Ice–chloroform–carbon tetrachloride mush and at −33° by refluxing ammonia.

To remove a sample, stirring was stopped for about a minute and enough hydrocarbon layer was removed with a pipet for infrared analysis. Cessation of stirring apparently brought the reaction nearly to a dead stop. The hydrocarbon layer was run onto a 30% solution of potassium hydroxide. The considerable warming which occurred indicates, in contrast to the case with sulfuric acid,

some solubility of the acid in hydrocarbon. To avoid possible side reactions, the hydrocarbon layer was run into the potassium hydroxide solution at −78°. This was then allowed to warm slowly.

Infrared analysis was by the procedures described for sulfuric acid.[2] It was assumed that the only isomerization product of 3-methylhexane was 2-methylhexane. The spread in the % isomerization computed at the five different wave lengths was small. For the purposes of this research, ignoring possible dimethylpentanes occasions no difficulty. The probable error in % 2-methylhexane is about 0.3 mole %.

Results

The data can be represented by the first-order equations

$$- \ln (1 - X_2/X_2{}^{eq}) = k_i t \qquad (1)$$

$$- \ln (1 - \Delta\beta/\alpha_0) = k_R t \qquad (2)$$

In these, X_2 is the mole fraction of 2-methylhexane, β is the rotation and $\beta_0 \equiv \alpha_0$ is the rotation of the initial 3-methylhexane. Rate constants are expressed in sec.$^{-1}$.

At −78° with halosulfonic acids and at 0° with chlorosulfonic acid–sulfuric acid mixtures, there seemed to be an induction period of the order of a few minutes and probably also at 30° with 100% sulfuric acid. The values of $X_2{}^{eq}$ are:[4] −78°, 0.702 (extrapolated from data at higher temperatures); −33°, 0.655; 0°, 0.628 and 30°, 0.612.

Since removal of alkane increases the proportion of acid, apparent values of the rate constants should increase after each removal of an alkane sample. This effect is small for the first two or three samples and has been ignored.

At −78°, extents of isomerization at very extensive losses in rotation were only 5 to 10%. Thus, accuracy in k_i is low. The same is true for many runs at −33°. Data are presented in Table I.

Although redistilled commercial chlorosulfonic acid exhibited the same pattern of behavior as the presumably purer synthetic material, the former resulted in much higher rates (run H vs. I). On the assumption that the redistilled commercial acid contained an impurity which accelerated reaction, the effect of the addition of small amounts of possible decomposition products of chlorosulfonic acid[5] and also addition of bromine and hydrogen bromide was investigated on rates of reaction with freshly distilled synthetic acid. Results are presented in Table II.

(1) G. S. Gordon, III, and R. L. Burwell, Jr., THIS JOURNAL, **71**, 2355 (1949).

(2) R. L. Burwell, Jr., R. B. Scott, L. G. Maury and A. S. Hussey, *ibid.*, **76**, 5822 (1954).

(3) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. X, Longmans, Green and Company, New York, N. Y., 1930, p. 686.

(4) L. G. Maury, R. L. Burwell, Jr., and R. H. Tuxworth, THIS JOURNAL, **76**, 5831 (1954).

(5) O. Ruff, *Ber.*, **34**, 3509 (1901).

TABLE 1

ISOMERIZATION AND RACEMIZATION OF (+)3-METHYLHEXANE

Run	Acid	Stirring	$k_R \times 10^6$	$k_i \times 10^6$	k_R/k_i
		Temperature −78°			
A	HClSO$_3$	Standard	33.4	1.0	33
A′	HClSO$_3$[a]	Standard	28.2	(0.4)	(70)
B	HFSO$_3$	Standard	33.4	1.0	33
C	HClSO$_3$	Rapid	51.1	1.0	51
D	HFSO$_3$	Standard[c]	2.5	0.5	5
		Temperature −33°			
G	HClSO$_3$	Slow[d]	6.7	4.3	1.6
H	HClSO$_3$	Standard	370	23.4	16
I	HClSO$_3$[b]	Standard	33.6	1.7	20
J	HFSO$_3$	Standard	1050	210	5.0
K	HFSO$_3$	Standard[c]	61	29	2.1
L	HClSO$_3$[b]	Rapid	42	1.8	24
		Temperature 0°			
M	HClSO$_3$–H$_2$SO$_4$[e]	Standard	116	40	2.9
N	HClSO$_3$–H$_2$SO$_4$[e]	Rapid	121	39	3.1
P[f]	96% H$_2$SO$_4$	Standard	0.043	0.033	1.3
		Temperature 30°			
Q	100% H$_2$SO$_4$	Rapid	30.4	21.4	1.42
R	100% H$_2$SO$_4$	Standard	25.3	18.3	1.38
S[f]	96% H$_2$SO$_4$	Standard	0.54	0.53	1.02

[a] A different sample of commercial acid from the others. Precision in k_i is low since X_2 was only 0.009.   [b] Synthetic HClSO$_3$.   [c] Standard stirring at half usual speed.   [d] Stirring with a mechanical, propeller-like stirrer. It gave a much poorer "emulsion" than *standard*.   [e] An equimolar mixture.   [f] These values are computed from data at a single point assuming no induction period: 0°, X_2 = 0.058, $\Delta\beta/\alpha_0$ = 0.118 at 81 hours and 30°, 0.067, 0.111 at 6 hours. Ignoring any induction period should not affect k_R/k_i, but owing to the small value of X_2 the ratio is of low precision.

TABLE II

EFFECT OF ADDED SUBSTANCES ON k_R AT −33°

Added material	$k_R \times 10^6$
None	42
4.5% SO$_2$Cl$_2$	46
1.5 Cl$_2$	0
2.0% Br$_2$	0
2.6% HCl	100
3.2% HBr	39
5.0% SO$_3$	55
3.0% SO$_2$	44

Discussion

A model has been proposed for the action of 96% sulfuric acid on (+)3-methylhexane at 60° in which the carbonium ion, $\text{CC}\overset{+}{\text{C}}\text{CCC}$, formed from 3-methylhexane by hydride ion transfer either to sulfuric acid or to another carbonium ion, isomerizes rapidly to an equilibrium mixture of this ion and the corresponding one derived from 2-methylhexane. The carbonium ions then abstract hydride ions from the tertiary positions of alkanes at such rates as to form 2- and 3-methylhexane in their equilibrium ratio.[2] Thus, the rate constants of loss of rotation and isomerization expressed by equations 1 and 2 should be equal for the sulfuric acid case. When values of X_2 are computed ignoring dimethylpentanes, the ratio k_R/k_i is actually about 0.9 at 60°.

As shown in Table I, at low temperatures with chlorosulfonic acids, the rate of loss of rotation much exceeds that of isomerization. With sufficiently good stirring, the ratio of the rate constants reaches 51 at −78° and 24 at −33°. We propose,

under these conditions, that the rate of hydride ion transfer considerably exceeds that of carbonium ion isomerization. Thus, carbonium ions formed from (+)3-methylhexane largely revert to (±)3-methylhexane and the over-all reaction closely approaches a pure racemization. This modification of the mechanism for sulfuric acid at 60° seems necessary and sufficient to accommodate the present data.

The representation of the chain-carrying species as a carbonium ion is convenient but not essential to the general application of the mechanism.

The behavior of fluorosulfonic acid resembles that of chlorosulfonic acid. Roebuck and Evering[6] have reported the isomerizing activity of fluorosulfonic acid.

As is the case with sulfuric acid,[2] it is difficult to decide whether chain initiation and hydride ion transfer occur at the hydrocarbon interface or whether they involve alkane dissolved in the acid layer.[7] Isomerization of carbonium ions and chain termination most likely occur in the acid phase.

With sulfuric acid at 60°, the ratio k_R/k_i is independent of stirring. As shown in Table I (compare runs A and C, B and D, G and H), k_R/k_i increases markedly with improved stirring at −78 and −33°. A smaller effect is noticed at higher temperatures but in these cases variation in stirring was less extensive. In general, the lower the temperature, the larger the value of k_R/k_i.

(6) A. K. Roebuck and B. L. Evering, THIS JOURNAL, 75, 1631 (1953).

(7) An earlier suggestion[1] that these reactions occur in the hydrocarbon phase is not now tenable.[2]

If all reactions occur in the acid phase, improved stirring causes a more rapid interchange of alkane between the acid and the hydrocarbon phase and causes the concentration of alkane in the acid phase to approach the equilibrium solubility. If the true rate of the hydride transfer reaction in the acid phase is more rapid than that of isomerization, both consequences of improved stirring will lead to greater increase in the observed rate of loss of rotation than in the observed rate of isomerization.

If, however, the isomerization were to occur in the acid phase and hydride ion transfer at the hydrocarbon–acid interface, then the increased extent of interface consequent to improved stirring could lead to the same result. However, results could hardly follow from a process in which both isomerization and hydride ion transfer occur at the interface.

From the decrease in the value of k_R/k_i with temperature, the activation energy of the isomerization reaction appears to exceed that of hydride ion transfer by a few kcal. In our mechanism, we have assumed that isotopic exchange is confined to hydrogen atoms adjacent to the tertiary position where any deuterated carbonium ion can undergo hydride ion transfer to form the correspondingly exchanged methylhexane. Thus, the relative extent of deuteration should decrease with decreasing isomerization but only to a lower limit corresponding to the exchange of seven hydrogen atoms (the number adjacent to the tertiary position of 3-methylhexane) provided isotopic exchange is fast compared with hydride ion transfer as at 60° with sulfuric acid. Actually[1] the relative extent of isotopic exchange goes to very low values with
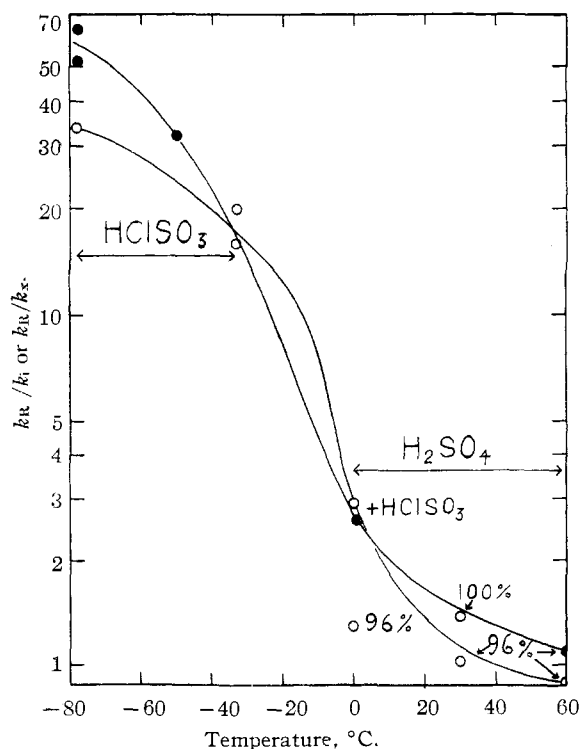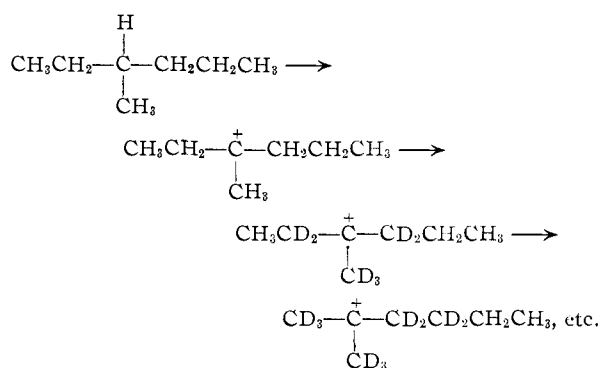
$$\begin{array}{c} \overset{\displaystyle H}{|} \\ CH_3CH_2-\overset{|}{\underset{|}{C}}-CH_2CH_2CH_3 \longrightarrow \\ \overset{|}{CH_3} \end{array}$$

$$\begin{array}{c} CH_3CH_2-\overset{+}{\underset{|}{C}}-CH_2CH_2CH_3 \longrightarrow \\ \overset{|}{CH_3} \end{array}$$

$$\begin{array}{c} CH_3CD_2-\overset{+}{\underset{|}{C}}-CD_2CH_2CH_3 \longrightarrow \\ \overset{|}{CD_3} \end{array}$$

$$\begin{array}{c} CD_3-\overset{+}{\underset{|}{C}}-CD_2CD_2CH_2CH_3, \text{ etc.} \\ \overset{|}{CD_3} \end{array}$$
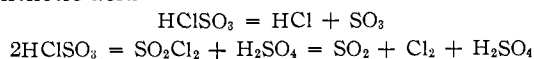
chlorosulfonic acid at low temperatures paralleling the decline in relative rate of isomerization. This is shown in Fig. 1 where the ratios of the rate constants of loss of rotation and exchange[1] are plotted as a function of temperature. Thus, the actual rate of exchange of the chain propagating species (here treated as a carbonium ion) falls with decreasing temperature relative to hydride ion transfer. The isotopic exchange might occur consequent to the isomerization process itself but such an assumption is difficult to reconcile with the isotopic exchange patterns observed with D_2SO_4.[8]

In the discussion above, we have interpreted the changes in relative rates on the basis of temperature coefficients of the primary reactions and have ignored medium effects. This is an over-simplification as comparison of runs P and S in Table I with other runs at the same temperatures shows. The difference between 96 and 100% sulfuric acid accords with the isotopic exchange patterns reported by Stevenson, et al.[8]

By suitable choice of acid and temperature, one may secure any situation intermediate between that in which the carbonium ions come to equilibrium with respect to simple methyl shift (96% sulfuric acid at 60°) and that in which hydride ion transfer is so much more rapid than isomerization to that one deals with a nearly pure racemization (chlorosulfonic acid at −78°).

The origin of the much greater rates of reaction with halosulfonic acids than with sulfuric acid may be compounded from the following factors: greater solubility of hydrocarbons in halosulfonic acid, greater oxidizing potential of halosulfonic acids, larger pK_a of halosulfonic acids. One would expect replacement of HO– by F– or Cl– to increase acidity. If tertiary esters form storage depots for carbonium ions, halosulfonate esters would presumably decompose to carbonium ions more rapidly than would bisulfate esters for the same reasons that the halosulfonic acids themselves deliver protons more readily.

Redistilled commercial chlorosulfonic acid exhibited much greater rates of loss of rotation than presumably purer synthetic material (runs H vs. I of Table I). None of the products of the following decomposition reactions led to activities equal to that of the commercial acid when added to the synthetic acid

$$HClSO_3 = HCl + SO_3$$
$$2HClSO_3 = SO_2Cl_2 + H_2SO_4 = SO_2 + Cl_2 + H_2SO_4$$

Fig. 1.—k_R/k_i and k_R/k_x as a function of temperature, where k_x is the rate constant of the isotope exchange reaction.

(8) D. P. Stevenson, C. D. Wagner, O. Beeck and J. W. Otvos, THIS JOURNAL, 74, 3269 (1952).

although hydrogen chloride did lead to some increase in rate. The synthetic acid may, of course, have contained some chain-stopping impurity to a greater extent than the presumably less pure commercial acid.

Chlorine and bromine bring the reaction to a dead stop. Presumably, they react with tertiary carbonium ions with the formation of tertiary halides and cut the chain length drastically. The chain length with pure chlorosulfonic acid must be long since the loss of rotation follows first-order kinetics to large losses in rotation.

Below 30°, chlorosulfonic acid and chloroform are miscible. No reaction is observed in such a solution in several days at room temperature. A mixture of chlorosulfonic acid (1.4 parts), chloroform (3 parts) and (+)3-methylhexane (1 part) is also homogeneous at 0° and 25°. However, the mixture becomes orange and evolves sulfur dioxide. After a reaction period at 0°, such a solution was neutralized with alcoholic potassium hydroxide at −33° and washed several times with cold, concentrated sulfuric acid. Upon treatment of the acid-washed material with alcoholic silver nitrate, a dense, white precipitate was formed. The filtered solution was washed with sulfuric acid to remove alcohol. With a reaction period of ten minutes at 0° negligible change in rotation occurred; in one hour, the rotation of the chloroform–hydrocarbon solution declined from 1.44 to 1.21°.

The failure of a reaction of long chain length to occur may be associated with the decreased dielectric constant of the medium and with reaction of any carbonium ions with either chlorosulfonic acid or chloroform to form the tertiary chlorides which appear to be present.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Equilibrium in the System 2- and 3-Methylhexane and in the System 2,3- and 2,4-Dimethylpentane

BY LUCIEN G. MAURY,[1] ROBERT L. BURWELL, JR., AND RICHARD H. TUXWORTH

Equilibrium constants for the reactions 3-methylhexane $\rightleftarrows$ 2-methylhexane and 2,3-dimethylpentane $\rightleftarrows$ 2,4-dimethylpentane, are: 1.47, 1.48 (60°); 1.69, 2.40 (0°); and 1.90, 2.68 (−33.4°). These values were determined by direct equilibration employing sulfuric acid at 60°, chlorosulfonic acid at −33.4° and an equimolar mixture of the two at 0°.

Sulfuric acid and chlorosulfonic acid specifically interconvert methylalkanes.[2−4] Change of chain branching as in the conversion of the 2- and 3-methylhexane pair to the 2,3- and 2,4-dimethylpentane pair occurs much more slowly. It, thus, seemed desirable to test the applicability of this discovery to the determination of the equilibrium constants of the following two reactions by direct equilibration

$$\text{3-methylhexane} \rightleftarrows \text{2-methylhexane} \qquad (1)$$

$$\text{2,3-dimethylpentane} \rightleftarrows \text{2,4-dimethylpentane} \qquad (2)$$
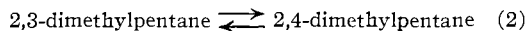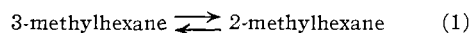
Voorthuijsen[5] determined the equilibrium constants of these reactions by direct equilibration of all heptanes by aluminum chloride at 20°. The more specific nature of the reaction with sulfuric acid offered hope of increased accuracy. The equilibrium constants have accordingly been measured at 60, 0 and −33.4°.

Experimental

The preparation of the hydrocarbons has been described.[3] The infrared absorption spectra were indistinguishable from those of the Bureau of Standards standard samples and no ultraviolet absorption was exhibited at wave lengths longer than 2200 Å.

As isomerizing agents, 96.04% sulfuric acid was employed at 60°, an equimolar mixture of this acid and freshly distilled Eastman Kodak Practical Grade chlorosulfonic acid was employed at 0°, and the chlorosulfonic acid alone was employed at −33.4°. Thermostating was by a water-bath at 60°, by an ice–water mixture at 0° and by refluxing ammonia at −33.4°.

The value of the equilibrium constant was first approximated from the relative *initial* rates of isomerization of the two hydrocarbons by the relation $K = k_1/k_{-1}$. Mixtures of known composition on either side of the estimated equilibrium composition were prepared and subjected to the isomerizing conditions. According to the observed changes in composition, the estimated equilibrium composition was revised and new mixtures prepared. These were then subjected to isomerizing conditions. By this means, it was possible to employ short times of contact and relatively mild condition and, thus, to minimize side reactions.

Reaction flasks and stirring procedures have been described.[3] To avoid preferential vapor loss of one component, ratios of gas to liquid volume were kept low, never exceeding 15 to 1.

The flask and acid were brought to temperature before the hydrocarbon mixture was added. After "emulsification" by magnetic stirring for the desired time, stirring was stopped and a sample of the hydrocarbon layer was pipetted into a cold 30% solution of potassium hydroxide. The hydrocarbon layer was then removed and stored over solid potassium hydroxide before analysis. Precautions were taken throughout to prevent change in composition of the hydrocarbon sample after removal from the thermostated reactor either by isomerization or preferential vapor loss.

Analysis.—An infrared spectrometric technique was employed[3] using a pair of matched cells and substitution against a standard mixture. As appropriate, this was

(1) Standard Oil Company (Indiana) Fellow, 1950–1951.

(2) R. L. Burwell, Jr., and G. S. Gordon, III, THIS JOURNAL, **70**, 3128 (1948); G. S. Gordon, III, and R. L. Burwell, *ibid.*, **71**, 2355 (1949).

(3) R. L. Burwell, Jr., Robert B. Scott, Lucien G. Maury and Allen S. Hussey, *ibid.*, **76**, 5822 (1954).

(4) R. L. Burwell, Jr., Lucien G. Maury and Robert B. Scott, *ibid.*, **76**, 5828 (1954).

(5) J. J. B. Voorthuijsen, *Rec. trav. chim.*, **66**, 323 (1947).