Hydride Transfer Reactions in Concentrated Sulfuric Acid

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Hydride transfer between *t*-butyl carbonium ions and several donors in concentrated sulfuric acid has been studied. The reaction appears to predominate at the interface, is first order in ion and donor concentration, and is subject to large steric requirements.

Hydride transfer reactions between aliphatic carbonium ions and paraffins in the presence of strong acids have been well documented since the work of Bartlett, Condon, and Schneider[1] with aluminum bromide. Similarly, hydride transfer in sulfuric acid is well recognized as an important step in carbonium ion processes involving saturated hydrocarbons. For example, abundant evidence exists[2-4] which indicates that abstraction of a hydride ion by a tertiary carbonium ion is a slow process compared with intramolecular rearrangement, proton loss, or addition to olefin, and therefore may be rate determining in the reactions of branched paraffins in sulfuric acid.

Despite our cognizance of the importance of hydride transfer, little information is available concerning the energetics of the process, or even of the phase in which reaction occurs. This paper deals with these problems and in particular with the reaction of *t*-butyl carbonium ions with hydride transfer agents in concentrated sulfuric acid.

Experimental

Hydride transfers were studied by adding *t*-butyl chloride to rapidly stirred solutions of sulfuric acid and the hydride donor. The reaction was followed manometrically in a large ballasted system (Figure 1). The apparatus contained a 500-ml. four-neck reactor fitted with a stirrer, and lines to a 5-l. ballast flask, a gas collection system, and an inlet system. The inlet system contained a hopper which permitted the essentially instantaneous addition of *t*-butyl chloride to the acid emulsion. Before adding the halide, the stirring speed was preset and the system was purged with nitrogen and leak tested. Readings were taken every 5 sec. for the first minute and more slowly throughout the rest of the experiment. Reactions were carried out at 10° with 250 ml. of acid. The volume of the empty system was calibrated as 6167 ± 3 ml. Gaseous products at the end of the run were passed through a caustic scrubber for halide determination. The hydrocarbons themselves were analyzed by gas chromatography and mass spectroscopy. Liquid products which separated from the acid after reaction were also analyzed by gas chromatography to determine if their distribution varied with the efficiency of the hydride donor.

The evolution of gaseous products always showed several characteristic regions (Figure 2), an immediate evolution of gas (I) followed by a transition to a fairly linear pressure–time curve (II) and then a decay toward some maximum pressure level (III). In order to obtain a clearer picture of the reactions involved, a sampling line connected to a Bendix Time-of-Flight mass spectrometer was added to the reaction system. This modification permitted the analysis of gaseous products formed throughout all portions of the reaction. These analyses provide accurate descriptions of the hydrocarbons, but they do not give reliable information concerning the HCl yield. This is presumably because of difficulties associated with the strong absorption of HCl on the walls of the spectrometer.

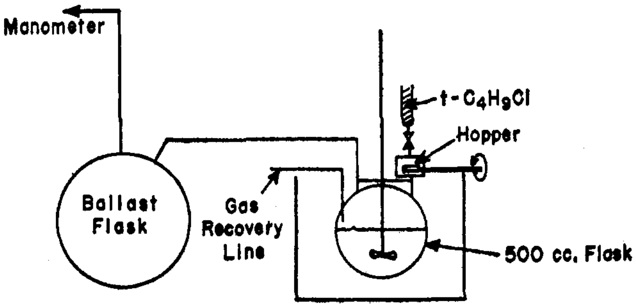

Figure 1.—Apparatus for hydride transfer studies.

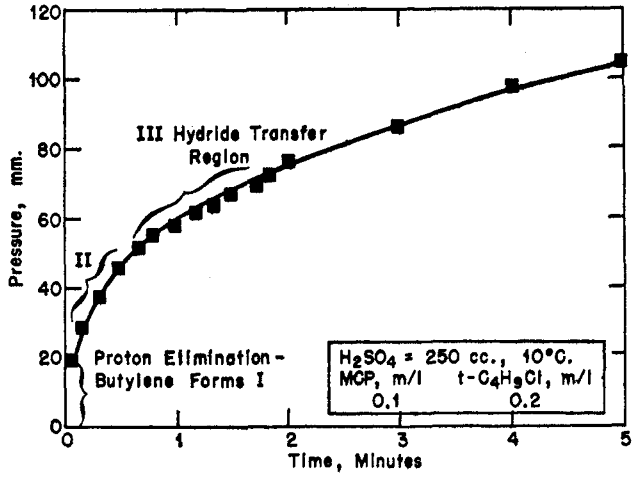

Figure 2.—Hydride transfer appears in a distinct region of a pressure–time plot.

The rate of pressure rise in region III was taken as a measure of the hydride transfer rate for kinetic analysis. The initial rate in this region in millimeters per minute was estimated from the pressure–time graph. It could be determined to about ±10% as indicated by the error spread on the methylcyclopentane data in Figure 6. The error is minimal at the conditions shown in Figure 2 in which the essentially linear pressure-time region which was taken at the initial rate is apparent from 45 to 90 sec. after mixing reagents. Duplicate experiments yield rates which are reproducible within the ±10% error in the determination of an individual point at these and similar conditions.

Order determinations were made by plotting the log of the hydride transfer rate, normalized to a constant concentration of one reactant, against the log of the concentration of the other reactant and determining the slope. In determining the order with respect to *t*-butyl chloride, the concentration of methylcyclopentane in the emulsion was held constant and, while determining the order with respect to methylcyclopentane, the concentration of *t*-butyl chloride added to the acid was kept constant.

The hydride donors, methylcyclopentane and methylcyclohexane, were washed with 96% sulfuric acid to remove olefinic impurities before use.

The solubility of methylcyclopentane and methylcyclohexane in sulfuric acid was determined by the following procedure. The hydrocarbon was acid washed in 96% H_2SO_4, separated, and

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[1] P. D. Bartlett, F. E. Condon and A. Schneider, *J. Am. Chem. Soc.*, **66**, 1531–1539 (1944).

[2] R. L. Burwell and G. S. Gordon, III, *ibid.*, **70**, 3128–3132 (1948).

[3] F. E. Condon and P. H. Emmett, "Catalysis," Vol. VI, Reinhold Publishing Corp., New York, N. Y.

[4] J. E. Hofmann and A. Schriesheim, *J. Am. Chem. Soc.*, **84**, 953 (1962), ref. 7 therein.

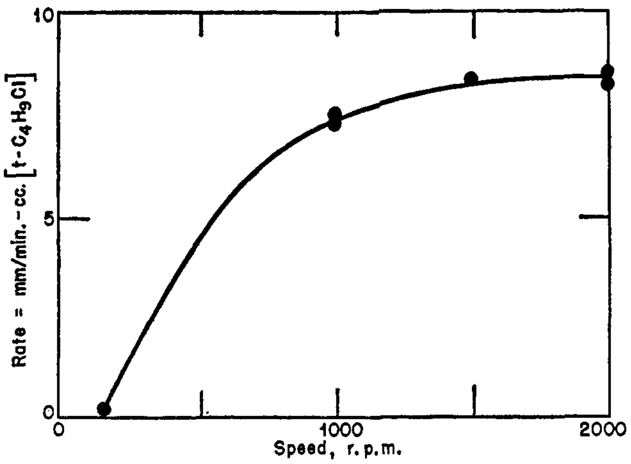


Figure 3.—Effect of stirring speed on hydride transfer (with MCP).

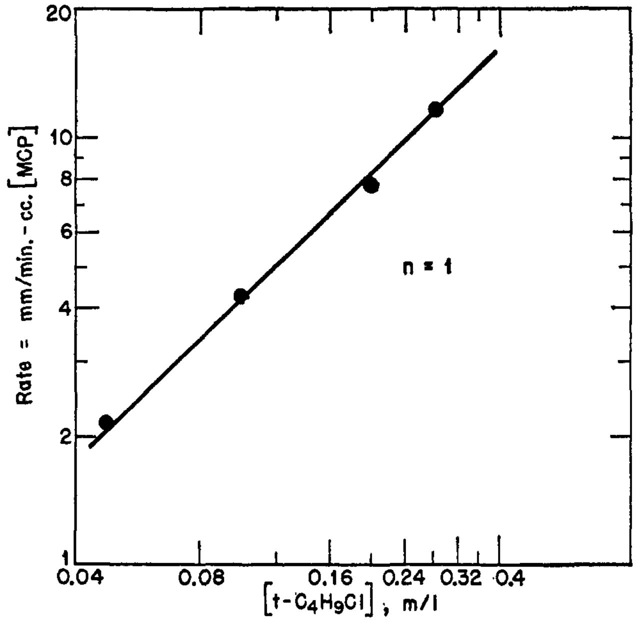


Figure 4.—Hydride transfer is first order in [t-C_4H_9Cl].

then added to fresh 96% acid, (about 10 ml. of hydrocarbon to 250 ml. of acid). This solution was vigorously shaken, and then allowed to settle for 24 hr. A 100-ml. aliquot of the acid layer was carefully withdrawn and extracted with three 10-ml. portions of carbon tetrachloride. The extracts were analyzed by infrared spectroscopy for the major bonds characteristic of the hydrocarbon.

Results

The rate of gas formation was found to depend on the *t*-butyl chloride and hydride donor concentrations at sufficiently high mixing speeds. At low speeds the reaction appears to be limited by the rate at which *t*-butyl chloride reaches the interface (Figure 3). To study the hydride transfer reaction and avoid this effect, all runs were carried out at 1000 r.p.m.

Isobutylene is the predominant product during the first 5–10 seconds of reaction. No isobutylene is present after 1 min. when isobutane and HCl are the only products in greater than trace quantities. The relative amount of HCl being formed at a given instant is not obtainable from our mass spectrometer studies because of its tendency to stick to the walls of the spectrometer. However, chemical analyses of all of the gaseous products evolved at the end of an experiment indicate ~4 : 1 HCl–isobutane ratios.

The reactions were found to exhibit a first-order dependence on *t*-butyl chloride (Figure 4) and on the methylcyclopentane concentration in the acid emulsion (Figure 5). The solubility of methylcyclopentane at 25° was determined to be 60 p.p.m. in 96% H_2SO_4 by extraction with CCl_4 and infrared examination. Accordingly, the acid must be considered saturated at all times.

In the absence of any donor, isobutane and HCl are still formed. The formation of isobutane indicates the formation of a hydride donor during the reaction. This is probably isobutylene formed by proton loss from a *t*-butyl carbonium ion. Notwithstanding, saturation by this path is slow compared with transfer from methylcyclopentane and does not materially affect our conclusions.

An activation energy of 9.9 kcal./mol was found for the reaction with methylcyclopentane (Figure 6). On the other hand, transfer from methylcyclohexane, which has a solubility of *ca.* 50 p.p.m., had an activation energy of 21.3 kcal./mole (Figure 6). These values were obtained between 10 and 30° and are good to ± 2.5 kcal.

An additional manifestation of the dependence of hydride transfer rates on donor concentration in the acid emulsion is obtained from an analysis of the small amount of by-products formed during reaction. The by-products are mainly octanes formed by self-alkylation of butyl carbonium ions and butenes with which they are in equilibrium. By increasing the methylcyclopentane to *t*-butyl chloride ratio it is possible to saturate trimethylpentyl ions somewhat more efficiently and alter the distribution of the octane fraction. Thus, the trimethylpentanes increased from 84 to 87–88% of the octane fraction as the methylcyclopentane–*t*-butyl chloride mole ratio was raised from 0.25 : 1 to 1 : 1.

Discussion

Several facets of hydride transfer to a tertiary carbonium ion in concentrated sulfuric acid may be inferred from our data. One of these is that hydride transfer from a branched cycloalkane is predominantly a surface reaction which depends on the properties of the donor and the carbonium ion in a particular medium.

Evidence for a surface reaction comes from the effect of stirring and the fact that the rate is a function of the concentration of donor, methylcyclopentane, in the emulsion. If the reaction were occurring homogeneously in the acid phase one would not expect to find any dependence on the bulk methylcyclopentane concentration since only ~60 p.p.m. methylcyclopentane will saturate fresh H_2SO_4, and the solution should be saturated at all times under the vigorous stirring conditions employed. On the other hand, a functional relationship between bulk donor concentration and rate would be consistent with an interfacial reaction.

This argument rests on the assumption that the concentration of methylcyclopentane in the bulk of the acid is constant, *i.e.*, that methylcyclopentane is able to diffuse through the hydrocarbon–acid interface considerably faster than it reacts. This appears to be a safe assumption based on the following order of magnitude estimation of the rate of diffusion. The rate of transport of methylcyclopentane in units of moles cm.$^{-2}$ sec.$^{-1}$, J, should be given by $-D\partial c/\partial x$ where D is the diffusion coefficient in cm.^{2} sec.$^{-1}$, c is in moles cm.$^{-3}$, and x is the thickness of an interfacial film in centimeters. Assuming the interfacial film to be between 10 and 100 Å. thick and that a normal D of 10^{-5} cm.^{2} sec.$^{-1}$ pertains leads to a minimum flow of 0.1 to 1.0 mole cm.$^{-2}$ sec.$^{-1}$. The minimum interfacial area in the 500-ml. reaction flask, no mixing, is 78 cm.^{2} corresponding to a minimum flow of 7.8 to 78 moles sec.$^{-1}$.

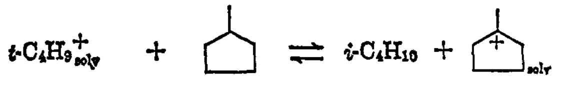
The maximum hydride transfer rate encountered in this work was much below 1000 mm. min.$^{-1}$ which is equivalent to 5×10^{-3} mole sec.$^{-1}$. The large difference between the estimated diffusion and maximum reaction rates is consistent with the postulate of an interfacial reaction.

The sequence of reactions occurring at the interface may be interpreted by the following carbonium ion mechanism (eq. 1–4). t-Butyl chloride is assumed to

$$\begin{tikzcd} t\text{-}C_4H_9Cl \arrow[d, "a"] & \\ t\text{-}C_4H_9^+Cl^- \arrow[r, "b"] \arrow[d, "c"'] & C_4H_8 + HCl \\ t\text{-}C_4H_9^+Cl^-_{solv} \arrow[r, rightleftharpoons, "d"] & t\text{-}C_4H_9^+{}_{solv} + Cl^-_{solv} \quad (1) \end{tikzcd}$$

$$t\text{-}C_4H_9^+{}_{solv} \rightleftharpoons i\text{-}C_4H_8 + H^+{}_{solv} \tag{2}$$

$$t\text{-}C_4H_9^+{}_{solv} + i\text{-}C_4H_8 \rightleftharpoons i\text{-}C_4H_{10} + i\text{-}C_4H_7^+{}_{solv} \tag{3}$$



(4)

ionize immediately upon mixing with sulfuric acid (a). Before the ion becomes fully solvated (c,d), some proton transfer to chloride ion or bisulfate ion occurs, which accounts for the large yield of isobutylene within 5 to 10 sec. of mixing reagents (b). The solvated ions rapidly establish an ion–olefin equilibrium in the acid (eq. 2). The carbonium ions then react with the various hydride sources.

According to the preceding mechanism the addition of t-butyl chloride to sulfuric acid is assumed to lead rapidly to a solution containing an equilibrium mixture of butyl ions and butylene. The concentrations of ions plus olefin is thus proportional to the amount of t-butyl chloride added. Since the ion–olefin equilibrium ought to be established rapidly, the initial ion concentration should also be proportional to the initial t-butyl chloride concentration. This proportionality rationalizes the experimental finding that the hydride transfer rate is first order in t-butyl chloride.

The large difference in activation energy for hydride transfer from methylcyclohexane as compared with methylcyclopentane (11 kcal./mole) is reasonable if reaction proceeds through a bimolecular transition state with large steric requirements. About 4 kcal./mole of this difference may be attributed to the comparative ease of forming the methylcyclopentyl and methylcyclohexyl ions by analogy with the relative ease of solvolyses of the corresponding 1-chloro-1-methylcycloalkanes.[5] The remaining difference may be largely attributed to the high degree of steric crowding in the transition state. Dreiding models indicate that attack of a t-butyl ion on equatorial methylcyclohexane, *i.e.*, on the axial hydrogen, leads to considerable interaction between a methyl group of the ion and the 3,5-axial hydrogens of methylcyclohexane. In this configuration, the interacting groups are nearly twice as close as in the corresponding attack on methylcyclopentane.

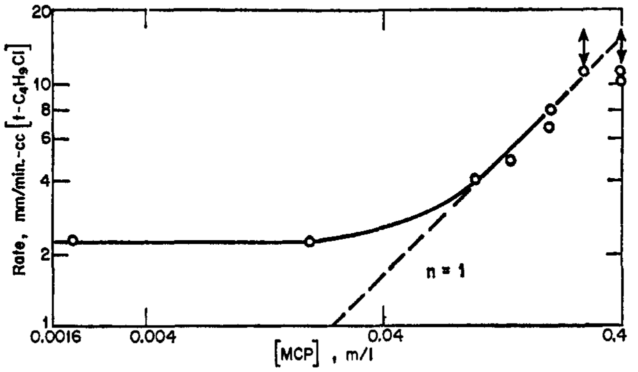


Figure 5.—Hydride transfer is first order in [MCP].

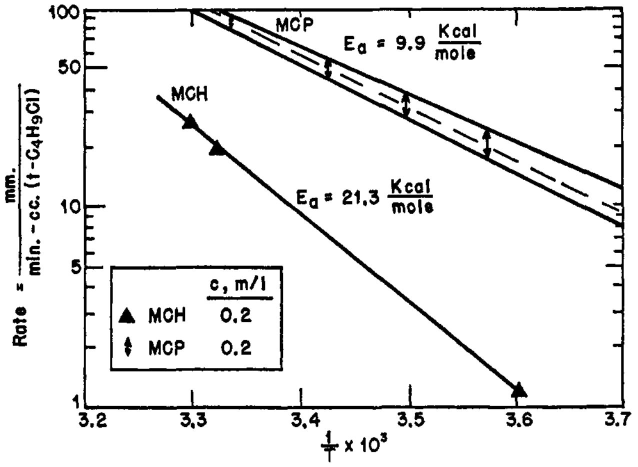


Figure 6.—Activation energies for hydride transfer from methylcyclohexane and methylcyclopentane differ by 11.4 kcal./mole.

Although it is difficult to estimate the magnitude of the steric requirements, it is clear that this effect is in the proper direction. This effect coupled with the greater driving force to ionization in the C_5 ring, therefore, seems responsible for the 11 kcal./mole difference in observed activation energy.

Acknowledgment.—We wish to thank Dr. A. Schriesheim and S. Bank for helpful discussions during this work and the Esso Research and Engineering Company for permission to publish these results.

[5] H. C. Brown and M. Berkowski, *J. Am. Chem. Soc.*, **74**, 1894 (1952).