The individual pentenes were identified by comparison of retention times with those of authentic A.P.I. isomeric pentenes.

Control Experiments.—A mixture of pentenes was analyzed, dissolved in ethanol, reseparated by the standard distillation procedure and reanalyzed. Within the experimental error (±0.5%) the mixtures gave identical analyses, showing that the distillation procedure separated the pentenes from the ethanol without fractionation of the pentenes themselves.

A mixture of pentenes was heated in the rate bath with ethanolic sodium ethoxide for a period of one week. Subsequent analysis showed no change in composition.

The uncorrected olefin compositions (base concentrations ~0.2 N, ester concentrations ~0.1 N) are listed in Table VI. The corrected olefin compositions are listed in Table IV.

TABLE VI

UNCORRECTED OLEFIN COMPOSITIONS FOR REACTION OF 0.1 N 2-PENTYL ARENESULFONATES WITH 0.2 N SODIUM ETHOXIDE IN ABSOLUTE ETHANOL

2-Pentyl sulfonate	$F_{trans\text{-2-pentene}}$	$F_{cis\text{-2-pentene}}$	$F_{1\text{-pentene}}$
p-Aminobenzene-	0.385	0.194	0.421
p-Methoxybenzene-	.394	.197	.409
p-Toluene-	.398	.199	.403
p-Bromobenzene-	.408	.199	.393
p-Nitrobenzene-	.425	.198	.377

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNA.]

Carbonium Ions. X. Hydride Transfers Involving Arylcarbonium and Alkylcarbonium Ions[1]

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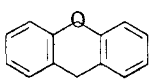
A linear relationship between log k and ΔpK_{R^+} was found by Dauben and McDonough (ref. 3) for three series of hydride transfer reactions. This same relation has now been found for the hydride transfer reaction between xanthene and a series of four triarylmethyl cations. For a given ΔpK_{R^+} value, the hydride transfer for xanthene is 10^3-10^4 faster to diarylmethyl cations than to triarylmethyl cations. For hydride transfers from aliphatic alcohols, esters and ethers to the diphenylmethyl cation, rates can be achieved in polyphosphoric acid that are at least 10^4 faster than in aqueous sulfuric acids. This effect is interpreted in terms of acidity functions. The acid-catalyzed equilibration of aliphatic alcohols and ketones has been observed. The failure of *t*-butyl alcohol to abstract hydride from xanthene in 55% H_2SO_4 is discussed.

Linear Free Energy Relations.—Dauben and McDonough[3] demonstrated that for three reaction series (triarylmethyl cations + cycloheptatriene, triarylmethyl cations + trianisylmethane and triphenylmethyl cation + triarylmethanes), each characterized by constant steric requirements at the reaction center, a plot of log k against ΔpK_{R^+} was linear. The symbol k is the rate constant and ΔpK_{R^+} is the difference in pK_{R^+} between the cation reacting and the cation forming.[4] For a given ΔpK_{R^+}, the rate of hydride transfer from cycloheptatriene to triarylmethyl cations was about 10^2 faster than for transfer between triarylmethyl systems.

The above kinetics were conducted in acetonitrile solutions using perchlorate salts of the cations. We have confirmed Dauben's relation using sulfuric acid solutions, xanthene (I) as the hydride donor and a series of four triarylmethyl cations. The data fit the linear equation log k = $0.76 \cdot (\Delta pK_{R^+}) - 2.86$, as shown in Table I. The rate constants for the six cations studied were invariant to at least 60% completion of the reaction and were independent of the concentrations of reactants. Triphenylmethyl cation showed no variation in k between 55 and 58% H_2SO_4 and 4-methoxytriphenylmethyl cation showed no variation in k between 45 and 50% H_2SO_4.[5]



I

TABLE I

RATE CONSTANTS FOR THE HYDRIDE TRANSFER REACTION BETWEEN XANTHENE AND ARYLALKYL CATIONS

Cation	Log k (k in l./mole sec.)	ΔpK_{R^+} [a]	Devn. in log k from correlating eq.
Triphenylmethyl	1.39	5.79	0.14
4-Methoxytriphenylmethyl	−0.907	2.56	0
4-Methyltriphenylmethyl	.593	4.40	−0.12
4,4′,4″-Trimethyltriphenylmethyl	− .807	2.72	0
4,4′-Dimethoxydiphenylmethyl	3.29	4.87	(−0.60)
1,1-Bis-(4′-methoxyphenyl)-ethyl	1.31	4.66	(−2.42)

[a] pK_{R^+} of xanthyl cation minus pK_{R^+} of the arylalkyl cation.

The linear relation between log k and ΔpK_{R^+} is equivalent to a linear relation between log k and σ^+ because ΔpK_{R^+} and σ^+ are linearly related.[6]

Steric Effects.—The steric effect of replacing one of the aryl groups on a triarylmethyl cation by first methyl and then hydrogen can be estimated from the data in Table I. Since pK_{R^+} for An_2CH^+

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(2) Research participant in the National Science Foundation program for college chemistry teachers.

(3) H. Dauben, Jr., and L. M. McDonough, Ph.D. Thesis of L. M., University of Washington, 1960.

(4) The method of evaluating pK_{R^+} is given in N. Deno, J. Jaruzelski and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955).

(5) Experimental details appeared in the Ph.D. Thesis of G. Saines, the Pennsylvania State University, 1961. The rates were followed spectroscopically using the λ_{max} of the triarylmethyl or diarylalkyl cation.

(6) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **79**, 1913 (1957); N. Deno and W. L. Evans, *ibid.*, **79**, 5804 (1957).

(An = anisyl) and $An_2C^+(CH_3)$ are close in value and since d log k/d ΔpK_{R^+} does not vary more than 2- to 3-fold for the reaction series studied, a measure of the steric effect is the difference between the observed log k for the diarylalkyl cation and the value estimated by the correlating equation for the triarylmethyl series, log k = 0.76 (ΔpK_{R^+}) − 2.86. Replacing aryl by methyl increases the rate (for constant ΔpK_{R^+}) 4-fold and replacing aryl by hydrogen increases the rate 3600-fold.

In the transition state of intermolecular hydride transfers, the $C^+–H^-–C^+$ system must be linear. Molecular models show that much deviation from linearity, particularly in the transfer of hydride between triarylmethyl cations, leads to interpenetration of atomic radii. For 1,5-transannular hydride shifts,[7,8] models indicate that a linear arrangement is most probable. This is in contrast to 1,2-intramolecular hydride shifts in which the C–H–C system must form a triangle.

Hydride Abstraction by Mineral Acids.—A major difficulty arose in studying the hydride transfer reactions in which xanthene acted as the hydride donor. The quantitative conversion of xanthene to xanthyl cation proceeds at appreciable rates in sulfuric acid concentrations as low as 55%. The rate of oxidation increases with acid concentration so that in 85% H_2SO_4 the oxidation of xanthene to xanthyl cation is instantaneous. In polyphosphoric acids from 60–83% P_2O_5, the rates were slow requiring hours for half completion of the oxidation. Similar oxidations to cations were found for 4,4′-dimethoxydiphenylmethane and 4,4′,4″-trimethoxytriphenylmethane in 60–80% H_2SO_4. In the polyphosphoric acid systems, the reaction may be a light-catalyzed air oxidation, since in 85% phosphoric acid degassing the system by repetitive freezing and evacuating combined with conducting the reaction in the dark led to marked reduction in the rate of oxidation. However, degassing and darkness were not effective in reducing the rate in 73% sulfuric acid.

Relative Rates in Polyphosphoric and Sulfuric Acids.—Bartlett and McCollum[9] reported that triphenylmethyl cation abstracted hydride from ethanol, 1-propanol, 2-methyl-1-propanol, 2-propanol, 2-butanol, 3-methyl-2-butanol, 3,3-dimethyl-2-butanol, diethyl ether and diisopropyl ether. Although methanol and dioxane failed to react, presumably they would also have donated hydride to the cation if it were possible to suppress their protonation while retaining the triphenylmethyl system in the cation form.

It is evident that to achieve hydride transfer with alcohols, esters and ethers, a system is needed which, relative to sulfuric acid, favors carbonium ion formation

$$ROH + H^+ = R^+ + H_2O$$

more than protonation

$$B + H^+ = BH^+$$

An obvious solution is to decrease the water activity and for this reason polyphosphoric acid systems were investigated. Qualitative indicator studies, summarized in Table II, showed that carbonium ion formation, as measured by the H_R acidity function, was favored relative to protonation, as measured by the H_0 function, when compared with sulfuric acid systems.[10]

TABLE II

APPROXIMATE H_R AND H_0 VALUES IN POLYPHOSPHORIC ACIDS

% P_2O_5 in water	$(-H_0)$[c]	% H_2SO_4 with same H_0 value	$-H_R$	% H_2SO_4 with same H_R value
61.5[a]	3.8	55	11	68
65.8	4	57	12.5	74
70.1	4	57	14	80
74.4	4	57	15	83
78.7	5.5	70	15	83
83.0[b]	7.5	81	16	87

[a] 85% H_3PO_4. [b] Commercial polyphosphoric acid. [c] These values are in agreement with those given in ref. 10.

Using the diphenylmethyl cation as the hydride acceptor, rates were measured in aqueous 83% H_2SO_4 and 72% P_2O_5. These acid concentrations were chosen as being somewhere near to the acidity for optimum rate.[11] The rate constant for 2-propanol, cyclopentanol, cyclohexanol, allyl alcohol, 1,2-dimethoxyethane, and dioxane were of the order of magnitude of 1 liter/mole sec. at 25°. Ethyl ether and 3-oxa-1,5-pentanediol were a factor of 5–10 slower. 2-Propyl benzoate and ethanol were about 1/100 as fast. Borneol, methyl benzoate, ethyl acetate, butyrolactone and valerolactone were so slow that reaction was not detected. In 83% H_2SO_4, every one of these compounds failed to show significant reaction rates so that these rate constants must be at least 10^{-4} smaller. All of the rates were followed spectroscopically using the 442 mμ λ_{max} of the diphenylmethyl cation.

With triphenylmethyl cation, the effect was less dramatic because the greater stability of this cation allowed the use of acid concentrations close to those in which free alcohol exists in comparable concentration with the protonated form. The rate constants were much smaller, in keeping with the greater steric hindrance and greater stability of the triphenylmethyl cation. 2-Propanol, cyclopentanol, cyclohexanol and allyl alcohol were oxidized in 62% H_2SO_4 at rate constants of the order of magnitude of 10^{-3} liter/mole sec. at 25°. The rates in 68% P_2O_5 were about twice as fast. The acid concentrations were chosen to give rapid rates, as with the diphenylmethyl cation.[11] All of the other compounds tested with the diphenylmethyl cation were also tested with triphenylmethyl cation in 62% H_2SO_4 and 68% P_2O_5, but

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(7) A. C. Cope, G. A. Berchtold, P. E. Peterson and S. H. Sharman, *J. Am. Chem. Soc.*, **82**, 6366 (1960).

(8) A. C. Cope, Abstracts of the Am. Chem. Soc. Meeting, March, 1961, p. 19-O; V. Prelog, *ibid.*, p. 20-O.

(9) P. D. Bartlett and J. D. McCollum, *ibid.*, **78**, 1441 (1956); for a more detailed study with 2-propanol, see S. G. Entelis, G. V. Epple and N. M. Chirkov, *Doklady Akad. Nauk*, **136**, 667 (1961).

(10) This accounts for the observation of D. E. Pearson (*J. Am. Chem. Soc.*, **83**, 1715, 1718 (1961)) that the rates of Beckmann rearrangements are much faster in polyphosphoric acid than in sulfuric acid solutions of the same H_0 value.

(11) The rate is proportional to the product of the concentrations of the reactants, R^+ and the hydride donor (ref. 9). The acid concentration at which this product maximizes can be computed using the H_0 function to calculate the concentration of hydride donor (free alcohol, ester or ether) and the H_R (C_0) function (ref. 4) to calculate c_{R^+}.

no significant reaction was detected. The rates were again followed spectroscopically using the 434 mμ λ_{max} of the triphenylmethyl cation.

The direction of hydride transfers gives an order of stability of carbonium ions based on extent of the reaction $RH = R^+ + H^-$. For example, CH_3CH^+OH and $CH_3CH^+OCH_2CH_3$ are more stable than triphenylmethyl cation.

Acid-catalyzed Equilibration of Aliphatic Ketones and Alcohols.—In refluxing 60% sulfuric acid, 2-butanone oxidized 2-propanol to acetone in a yield of 5%. Under the same conditions, cyclohexanone oxidized 2-propanol to acetone in 28% yield. Both yields are calculated on the basis of the 2-propanol added. Increasing the acid concentration to 65% or decreasing it to 55% reduced the yields of acetone. The acetone was continuously distilled off so that the yields do not represent concentrations present at equilibrium.

It was anticipated that the reaction would be most rapid in 60–65% H_2SO_4. From the pK for acetone,[12] the pK of 2-propanol[9] and the H_0 function, it was computed that the product of the concentrations of the reactants, protonated ketone and free alcohol, would maximize in that acidity, at least at 25°.

***t*-Alkyl Cations.**—An effort was made to detect hydride transfer between xanthene and simple aliphatic alkyl cations. With *t*-butyl alcohol, no reaction was observed in 55% H_2SO_4. In more concentrated acids, although abstraction of hydride by the *t*-butyl cation was overshadowed by the direct oxidation by the sulfuric acid, a trace of hydride transfer was detected.[13] Nitrogen was passed through a reaction mixture of xanthene and *t*-butyl alcohol in 75% H_2SO_4. Passage of the nitrogen stream through a liquid air trap and examining the condensate by vapor phase chromatography revealed the formation of a 0.06% yield of isobutane based on added xanthene. Isobutane was not formed when the xanthene was omitted.

2-Methyl-3-buten-2-ol was the one aliphatic alcohol of many tested that clearly formed a xanthyl cation from xanthene much faster than the direct oxidation. However, the reaction is complex since the absorption spectrum, although closely resembling xanthyl cation, had λ_{max} at 385 mμ instead of 375 mμ, suggesting that an alkylated xanthyl cation had been produced. The similar 2-methyl-3-penten-2-ol and 2,4-dimethyl-3-penten-2-ol failed to abstract hydride faster than the direct oxidation.

It is significant that *t*-butyl alcohol fails to abstract hydride from xanthene in 60% H_2SO_4. On the basis of alkylation of acrylonitrile studies[14] and by analogy to the protonation of 2-propanol,[9] *t*-butyl alcohol is half protonated in 56% H_2SO_4 and it is the generation of protonated *t*-butyl alcohol, $(CH_3)_3C\text{–}OH_2^+$, that quantitatively accounts for the acid catalysis in nitrile alkylation.[14] The encumbered carbonium ion proposed for the dehydration of *t*-butyl alcohol[15] is regarded by us as conceptually equivalent. The abundance of $(CH_3)_3C\text{–}OH_2^+$ in 60% H_2SO_4 and the failure to abstract hydride from xanthene in this acid means that protonated *t*-butyl alcohol, although capable of alkylating nitriles, dehydrating to olefins and exchanging O^{18},[15,16] is ineffective in hydride transfer reactions, presumably because it does not possess a sufficiently open sextet of electrons.

Hydride transfer reactions of the *t*-butyl system are found in concentrated sulfuric acid,[17] where the greatly lowered activity of water has shifted the equilibrium from $(CH_3)_3C\text{–}OH_2^+$ to $(CH_3)_3C^+$.

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[12] H. J. Campbell and J. T. Edward, *Can. J. Chem.*, **38**, 2109 (1960).

[13] These measurements were kindly made by Dr. H. Skovronek.

[14] N. Deno, T. Edwards and C. Perizzolo, *J. Am. Chem. Soc.*, **79**, 2108 (1957).

[15] R. H. Boyd, R. W. Taft, Jr., A. P. Wolf and D. R. Christman, *ibid.*, **82**, 4729 (1960).

[16] I. Dostrovsky and F. S. Klein, *J. Chem. Soc.*, 791, 4401 (1955).

[17] J. W. Otvos, D. P. Stevenson, C. D. Wagner and O. Beeck. *J. Am. Chem. Soc.*, **73**, 5741 (1951); *J. Chem. Phys.*, **17**, 419 (1949).