[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Hydride Transfer Mechanisms in Strongly Acid Media. The Reduction of Carbonium Ions by Alcohols and an Evaluation of the Basic Strength of Isopropyl Alcohol

BY PAUL D. BARTLETT AND JOHN D. MCCOLLUM

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Di-*p*-anisylcarbinol is disproportionated in a melt with trichloroacetic acid-*d* into *p,p'*-dimethoxybenzophenone and dianisylmethane containing no deuterium. Triphenylcarbinol is converted quantitatively, in the presence of 2-propanol-2*d* (87% D) in 50% sulfuric acid (by weight), into triphenylmethane containing 0.798 atom of deuterium per molecule. Therefore these oxidation–reduction reactions consist of hydride transfers from the α-position of an alcohol to the positively charged center in a carbonium ion. The disappearance of the color of the triphenylcarbonium and dianisylcarbonium ions in the presence of various alcohols has been followed kinetically in a series of sulfuric acid–water mixtures. It is a second-order reaction between carbonium ion and alcohol. In solutions where triphenylcarbinol is largely ionized, the rate of reaction is decreased with increasing sulfuric acid content, as the alcohol is converted increasingly into its oxonium ion. From the rate of reaction as a function of H_0 and the degree of carbinol ionization, it is possible to calculate the rate constant for hydride transfer from neutral alcohol to carbonium ion and also the pK_a of the alkyloxonium ion. The reaction shows an isotope effect k_H/k_D between 1.8 and 2.6. The rate of reaction yields a composite constant into which the basicity of the alcohol and the rate constant for hydride transfer by the pure neutral-base form of the alcohol both enter. For five alcohols and two ethers the composite $\Delta H^{\ddagger}$ is 14–19 kcal. and $\Delta S^{\ddagger}$ is -15 to -26 e.u. The basicity of isopropyl alcohol corresponds to a pK_a for isopropyloxonium ion of -3.2, indicating that isopropyl alcohol is less basic than water by a factor of about 290. Similar determinations of the basic strengths of other alcohols are in progress. Dioxane and methanol do not serve as donors of hydride ion at rates suitable for measurement under conditions favorable for the formation of the triphenylcarbonium ion. Dianisylcarbinol is converted by acetone to dianisyl ketone at values of H_0 less acid than -3. This reaction appears to be fully analogous to the carbinol–carbonyl interconversions observed in highly basic media. Small additions of alcohols produce large depressions of the indicator acidities of sulfuric acid–water mixtures, an effect which must be due to shifting activity coefficients of the indicator base and its conjugate acid, as recently observed by Paul and by McIntyre and Long for certain salts. Because of rapid acid-catalyzed rearrangement of triphenylmethyl hydroperoxide, strongly acid solutions of triphenylcarbinol are exceedingly sensitive to small amounts of hydrogen peroxide and other peroxides.

Introduction

Although free hydride ions are almost as elusive as free protons, hydride transfers have come to occupy a secure place, along with proton transfers, among the mechanisms of organic reactions. By a hydride transfer we mean the acquisition, in a single step, of a proton and two electrons by one electrophilic center at the expense of another, either in the same or in a different molecule. Two features distinguish hydride transfers from proton transfers: the nature of the polarity at the point of reaction, and the absence of isotope exchange between the transferred hydrogen and the hydroxyl groups of the reaction medium. Since it would always be possible for a transfer of H^- to occur in steps (an electron followed by a hydrogen atom), one looks also for any indications of free radical intervention in such processes.

Examples of hydride transfer range all the way from the Cannizzaro reaction[1,2] in strongly alkaline medium to the extremely rapid interchanges between isoparaffins and organic halides brought about by aluminum bromide or chloride.[3] The driving force for hydride transfer is derived at the one extreme from the negative charge on an alkoxyl ion which enables it to be stabilized with formation of a carbonyl group by the act of losing a hydride ion; at the other extreme the driving force comes from the positive charge on a reactive carbonium ion which drives the reaction by permitting the formation of a stable hydrocarbon. Intermediate between these extremes are such concerted processes as the Meerwein–Ponndorf–Verley and Oppenauer reactions, in which free ions are not involved, but in which the electrophilic activity of an aluminum atom and the nucleophilic character of alkoxide oxygen are simultaneously at work to facilitate hydride transfer.

Especially careful investigation has been devoted to the reversible hydride transfers between alkoxide ions and ketones or aldehydes.[4-6] In addition to stereochemical and isotopic studies reinforcing the proposed mechanism, Doering and Aschner showed that the active electron-transfer system of Bindschedler's Green was without effect upon the hydride-transfer reactions of *sec*-butylcarbinol and its aldehyde. There is thus no evidence that the proton and two electrons are transferred other than simultaneously.

In connection with our interest in hydride capture by carbonium ions we have sought examples of this process which should be amenable to kinetic study, since the rate measurements on hydrocarbon systems have left much to be desired. There are some familiar reactions of preparative chemistry which apparently proceed in this fashion, such as the alkylation of amines with aldehydes, with and without formic acid, or the reduction of triphenylmethyl chloride by ether in the presence of aluminum chloride.[7-9] The latter appears to be a general type of reaction[10] well adapted to rate studies, since under the conditions of the reaction the triphenylmethyl chloride is partially or wholly ionized

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(1) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 350.

(2) H. Fredenhagen and K. F. Bonhoeffer, *Z. physik. Chem.*, **A181**, 379 (1938).

(3) P. D. Bartlett, F. E. Condon and A. Schneider, THIS JOURNAL, **66**, 1531 (1944).

(4) R. B. Woodward, N. L. Wendler and F. J. Brutschy, *ibid.*, **67**, 1426 (1945).

(5) W. v. E. Doering, G. Cortes and L. H. Knox, *ibid.*, **69**, 1700 (1947).

(6) W. v. E. Doering and T. C. Aschner, *ibid.*, **71**, 838 (1949); **75**, 393 (1953).

(7) W. Eschweiler, *Ber.*, **38**, 880 (1905).

(8) R. Leuckart and co-workers, *ibid.*, **18**, 2341 (1885), and later papers.

(9) M. Sommelet and Ferrand, *Bull. soc. chim., France*, [4] **25**, 457 (1919).

(10) J. F. Norris, "Organic Syntheses," Coll. Vol. 1, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., p. 548.

to a colored carbonium ion, and this color disappears in the course of the reduction. Related examples include the reduction of xanthydrol by ethyl alcohol and hydrogen bromide,[11] of triphenylcarbinol and trixenylcarbinol by alcohols and ethers with sulfuric acid,[12] and of polymethoxytriphenylcarbinols by ethyl alcohol and hydrogen chloride.[13] Kny-Jones and Ward showed that on boiling in dilute hydrochloric acid, xanthydrol could serve as its own reductant, being converted quantitatively into xanthane and xanthone, a reaction which did not occur in the presence of sodium hydroxide.[14] Similar observations were made in the cases of dianisylcarbinol and phenylanisylcarbinol by Balfe, Kenyon and Thain,[15] who identified acetaldehyde and propionaldehyde among the products when ethyl and *n*-propyl alcohols were used, respectively, as reducing agents in the presence of hydrogen chloride, and who studied the disproportionation of these alcohols with trichloroacetic acid, molten or in an inert solvent. Benzhydrol is not disproportionated under these conditions, but is converted into diphenylmethane and benzophenone in the presence of perchloric acid.[16]

Product Study with Deuteriotrichloroacetic Acid.—Balfe, Kenyon and Thain obtained permissive evidence for the suggestion of Kny-Jones and Ward that these reactions proceeded by way of an ether. Ethers of dianisylcarbinol with itself or with the reductant alcohol were found among the products; introduced under the reacting conditions they led to the same products as were normally observed. Kenyon[15] and co-workers, however, proposed a mechanism for the hydrogen transfer which required that the new hydrogen atom in the dianisylmethane be delivered from the oxygen atom of dianisyloxonium ion, and hence arise from the dissociable hydrogen of the acid used. Such a mechanism can be tested by tracer experiments.

Dianisylcarbinol was disproportionated in a melt with an equimolar amount of trichloroacetic acid-*d*, prepared from trichloroacetic anhydride and 99.75% deuterium oxide. Dianisylmethane, isolated from the product in 30% yield, was burned and the water produced was analyzed by the gradient density method by Mr. R. P. Anderson. The hydrogen contained less than 0.02% deuterium. Allowing for dilution of the deuterium of the acid to 50% by exchange with the hydroxyl groups of the alcohol, any proton-transfer mechanism requires that the product methane contain between 0.45% (one atom in 224) and 3.12% (one atom in 32) of deuterium depending upon whether there is a sevenfold kinetic isotope effect favoring protium transfer over deuterium or no isotope effect at all. Thus the hydrogen atom which is delivered to one of the alcohol molecules to produce dianisylmethane comes from the reductant molecule without any interchange with the acidic hydrogen of the solvent. It is therefore not transferred as a proton.[17]

Product Study with Deuterioisopropyl Alcohol.—Acetone was reduced with lithium aluminum deuteride, the product decomposed with normal ethylene glycol, and the resulting 2-propanol-2*d* was found to contain 0.874 atom of deuterium per molecule. This labeled alcohol was used in tenfold excess to reduce triphenylcarbinol in a medium consisting of two parts by volume of sulfuric acid to one part of water. Triphenylmethane was isolated in a yield of 98%, m.p. 91–92°, and was found to contain 4.99 atom per cent. deuterium corresponding to 0.798 atom of deuterium per molecule. From the equation

$$\ln \frac{(\mathrm{C_3H_7OH})_0}{(\mathrm{C_3H_7OH})_0 - ((\mathrm{C_6H_5})_3\mathrm{CH})_\infty} = \frac{k_\mathrm{H}}{k_\mathrm{D}} \ln \frac{(\mathrm{C_3H_6DOH})_0}{(\mathrm{C_3H_6DOH})_0 - ((\mathrm{C_6H_5})_3\mathrm{CD})_\infty}$$

$k_\mathrm{H}/k_\mathrm{D}$ for this reaction is estimated to be 1.84. Again the non-exchange with the acidic hydrogen of the medium indicates that the hydrogen atom is not transferred as a proton, while the low value of the isotopic rate ratio is in common with other examples of transfer of hydrogen with negative polarity.[18] The triphenylmethane-*d* showed the peak at 4.78 μ characteristic of the C–D stretching vibration.

Acetone was recovered from a similar reaction in 55 weight per cent. sulfuric acid, after dilution, as the 2,4-dinitrophenylhydrazone in 65% yield.

Exploratory Kinetic Study of the Reaction of Arylcarbinols with Ethanol.—Exploratory experiments were carried out with triphenyl- and dianisylcarbinols dissolved in absolute ethanol containing from 22 to 40 volume per cent. of sulfuric acid. Concentrations of the carbinols from 10^{-5} to 10^{-4} *M* proved convenient for measurements of optical absorption, the maxima being at 430 and 500 mμ, respectively. Beer's law was found to be obeyed. The disappearance of color in these experiments showed a first-order dependence on time which was identical whether the starting material was triphenylcarbinol or triphenylmethyl ethyl ether. This indicates a rapid equilibration among the relevant species, which makes it impossible to determine whether carbinol, ether, sulfate or carbonium ion is the active participant in the reaction by simple comparison of their separate behavior. On the other hand, previous measurements in the literature indicate that the formation of *diethyl* ether should be slower than the reaction here observed by a factor of 10^6,[19] while the sulfation of alcohols should be slower than the reduction by a factor of 100 to 1000.[20] The high yield and purity of triphenylmethane under the conditions of acidity generally employed, as well as the fit of the observations to first-order kinetics, shows that alkylation of

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[11] R. Fosse, *Compt. rend.*, **133**, 100, 881 (1901); R. Fosse and P. Bertrand, *ibid.*, **139**, 601 (1904).

[12] J. Schmidlin and A. Garcia-Banûs, *Ber.*, **45**, 3188 (1912).

[13] H. Kauffmann and P. Pannwitz, *ibid.*, **45**, 766 (1912).

[14] F. G. Kny-Jones and A. M. Ward, *J. Chem. Soc.*, 535 (1930).

[15] M. P. Balfe, J. Kenyon and E. M. Thain, *ibid.*, 790 (1952).

[16] H. Burton and G. W. H. Cheeseman, *ibid.*, 986 (1953).

[17] A similar test has been reported by G. Baddeley and P. G. Nield, *ibid.*, 4684 (1954) (*cf.* G. Baddeley and W. Pickles, *ibid.*, 3728 (1953)) in the case of disproportionation of dibenzhydryl ether by $\mathrm{DClO_4}$.

[18] See, for example, L. Kaplan and K. E. Wilzbach, This Journal, **77**, 1297 (1955), and the discussion by P. D. Bartlett and F. A. Tate, *ibid.*, **75**, 95 (1953).

[19] A. Skrabal and R. Skrabal, *Z. physik. Chem.*, **A181**, 449 (1938).

[20] N. C. Deno and M. S. Newman, This Journal, **72**, 3852 (1950).

the aromatic rings is not competing with the reduction. In a few experiments in sulfuric acid of strength higher than 75%, deviations toward higher kinetic order may mean the simultaneous occurrence of alkylation. It was verified that neither acetone nor mesityl oxide had any effect upon the rate of the reaction (Fig. 1) between triphenylcarbinol and isopropyl alcohol.

Acid-Base and Dissociation Equilibria.—Both the arylcarbinols and the aliphatic alcohols are subject to protonation equilibria which will depend upon the acidity function (H_0) of the sulfuric acid-water mixture

$$ROH + HA \rightleftarrows ROH_2^+ + A^-$$

Because triphenylcarbinol yields a stable carbonium ion and the simple alcohols do not, the arylcarbinol and its relatives alone undergo a further dissociation

$$ROH_2^+ \rightleftarrows R^+ + H_2O$$

The extent to which ethyl, isopropyl and other simple alcohols are converted into their conjugate acids must depend upon the H_0 of the solution,[21] determined in the presence of any uncharged base as

$$H_0 = pK_a + \log_{10}(C_B/C_{BH^+})$$

The extent to which an arylcarbinol is converted into its carbonium ion should be similarly determined by the analogous function C_0[22,23]

$$C_0 = H_0 + \log_{10} a_{H_2O} + \log_{10}(f_{R^+}/f_{ROH_2^+})$$

which is the subject of a recent paper by Deno and co-workers.[22] Before the appearance of that paper, we measured the degree of ionization of triphenylcarbinol and dianisylcarbinol in a series of sulfuric acid-water mixtures. These carbinols are half converted to their colored forms at J_0 values of -4.18 and -2.79, respectively. We observed that for each carbinol the quantity $\log((R^+)/(ROH))$ was a linear function of J_0, but with slopes of 1.14 and 1.31, respectively, instead of unity as required by the equation of Gold and Hawes. This discrepancy is accounted for by the work of Deno, *et al.*, who have found that the ratio of activity coefficients of the two cations, R^+ and ROH_2^+, varies by almost five powers of ten over the range of sulfuric acid-water mixtures, whereas this ratio must be assumed to be constant for the simple J_0 treatment to be applicable.

Because the H_0 values of the solutions (and hence also their C_0 values) were markedly shifted by small additions of alcohols (see below) the fractional ionization of each arylcarbinol for the conditions of each experiment was read off from an experimental curve of $\log(\alpha/(1 - \alpha))$ (α = fraction ionized) against H_0, using the H_0 value determined by indicator for the solution in which each rate determination was to be made. With the assumption that the C_0 and H_0 of each acid mixture remains unchanged during a kinetic measurement, each rate of reaction observed can be divided by α, the fraction of triphenylcarbinol existing as carbonium ion, and so referred to this ionic species as reactant. The H_0 values of the sulfuric acid-water-alcohol mixtures were also determined with the use of two of Hammett's indicators. The results for isopropyl alcohol-containing solutions, which are numerically very close to those for solutions of the other alcohols used, are listed in Table I, and shown graphically in Fig. 2.

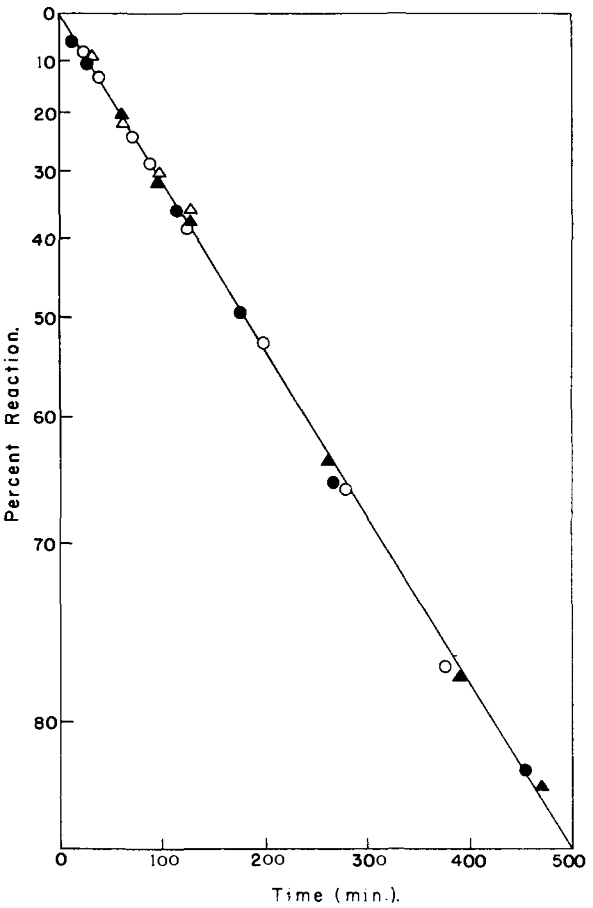

Fig. 1.—Reaction of Ph_3COH with 0.501 *M* *i*-PrOH: $H_0 = -3.68$; $T = 25.05°$; ○, nothing added; ▲, nothing added; ●, acetone; △, mesityl oxide.

Effect of Alcohols on Indicator Acidity.—It is noted that the H_0 of stock solution 6 has been made less negative, from -3.93 to a value of -3.63, by the addition of 0.621 mole per liter of isopropyl alcohol (Fig. 2). The concentration of water which it would have been necessary to add to achieve this same result is 6.7 moles per liter (Fig. 2). The addition of 0.621 mole per liter of sodium hydroxide would have been expected to change the H_0 only to -3.75, if we neglect any salt effect of the resulting sodium bisulfate. It is clear, then, that the effect of these increments of isopropyl alcohol upon the indicator acidity is a specific effect of the kind recently noted by Paul[24] and by McIntyre and Long.[25] Whereas the effect of most salts is to increase the indicator acidities of aqueous hydrochloric acid solutions (to make H_0 more negative), tetramethyl- and tetraethylammonium bromides have a strong contrary effect, which was shown to

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[21] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 267.

[22] N. C. Deno, J. J. Jaruzelski and Alan Schriesheim, THIS JOURNAL, **77**, 3044 (1955).

[23] Compare V. Gold and B. W. V. Hawes, *J. Chem. Soc.*, 2102 (1951), defining J_0.

[24] M. A. Paul, THIS JOURNAL, **76**, 3236 (1954).

[25] D. McIntyre and F. A. Long, *ibid.*, **76**, 3243 (1954).

TABLE I

DETERMINATION OF SOLUTION H_0 VALUES AT 25.0°

Acid stock soln.	Alcohol, mole/l.	Indicator, mole/ 1×10^5	Absorbance	$\epsilon_{app} \times 10^{-3}$	$\frac{\epsilon_{app}}{\epsilon - \epsilon_{app}}$	H_0
With 2,4-dichloro-6-nitroaniline at 425 mμ, $\epsilon = 2.85 \times 10^3$						
1	0.501	1.61	0.440	2.74	24.0	−1.84
2	.501	1.61	.335	2.08	2.71	−2.79
3	.501	1.61	.258	1.60	1.28	−3.11
4	.501	1.61	.217	1.35	0.896	−3.27
With 2,4-dinitroaniline at 410 mμ, $\epsilon = 4.95 \times 10^3$						
5	None					−3.86
	0.129	5.01	0.204	4.07	4.56	−3.71
	.256	4.96	.208	4.19	5.55	−3.64
	.380	4.92	.211	4.30	6.69	−3.55
	.501	4.88	.215	4.40	8.00	−3.48
	.621	4.82	.218	4.52	10.5	−3.36
With 2,4-dinitroaniline at 348 mμ, $\epsilon = 12.8 \times 10^3$						
6	None					−3.93
	0.129	5.01	0.495	9.88	3.39	−3.85
	.256	4.96	.503	10.9	3.76	−3.80
	.380	4.92	.510	10.4	4.26	−3.75
	.501	4.88	.519	10.6	5.05	−3.68
	.621	4.82	.524	10.9	5.66	−3.63
7	0.129	5.01	0.388	7.74	1.53	−4.19
	.256	4.96	.402	8.10	1.73	−4.14
	.380	4.92	.411	8.36	1.88	−4.10
	.501	4.88	418	8.57	2.02	−4.07
	.621	4.82	.427	8.86	2.25	−4.03
8	0.129	5.01	0.280	5.59	0.776	−4.48
	.256	4.96	.286	5.77	0.821	−4.45
	.380	4.92	.300	6.10	0.911	−4.41
	.501	4.88	.312	6.39	1.00	−4.38
	.621	4.82	.323	6.70	1.11	−4.34

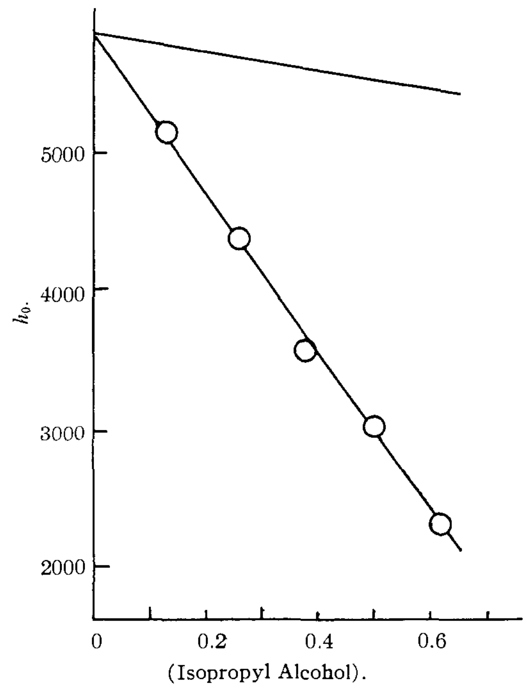

Fig. 2.—Points, effect of additions of isopropyl alcohol on indicator acidity of a sulfuric acid–water mixture; upper line, effect of additions of corresponding molar quantities of water to the same solution.

be due chiefly to a lowering of the activity coefficient (increase in solubility) of the neutral indicator base. The salts which show this effect have hydrocarbon-like organic cations which thus resemble the isopropyloxonium ion, the predominant form of isopropyl alcohol in solutions such as these. The magnitude of the depression of the indicator acidity by additions of isopropyl alcohol becomes steadily less from the less acidic to the more acidic sulfuric acid–water mixtures. This may be due in part to at least two factors. (1) Isopropyl alcohol may have a greater effect than its oxonium ion on the solubilization of the indicator base. (2) The effect of added electrolyte on the activity coefficients of the ionic species (which also contributes to the total effect) may become steadily less with increasing sulfuric acid content and approach to ideal behavior.

The serious disturbance of the indicator acidity which is produced by small additions of alcohols limits the interpretation of the results. The H_0 scale in sulfuric acid–water mixtures already has been shown to be useful for substrates of a variety of types, but when the medium is altered by addition of electrolytes, the response of various neutral bases varies considerably with their structure. In the present work the activity coefficients of three conjugate base–acid pairs are of importance: the indicator system used to determine the acidity function of a solution, the aryl carbinol with its carbonium ion, and the alcohol which is the source of the hydride ion transferred, together with its oxonium ion. We observed that the addition of the last-named component has large effects upon the activity coefficients of the indicator and its conjugate acid. We assume that the aryl carbinol and carbonium ion, the alcohol and its oxonium ion, have their activity coefficients affected in a similar way, so that the H_0 which is determined by the indicator is also appropriate for the other two systems. Any error in this assumption will be reflected in results which are increasingly inconsistent and unreliable, the larger the concentration of added alcohol. The trouble may well be most serious in the estimation of water activities, since we have determined the fraction $(T^+)/(TOH)$ in our solutions by interpolation on a plot of experimental values at H_0's determined before the additions of alcohol. In the following section we derive the equations which ideally should govern the rate of hydride transfer as a function of the H_0 of the medium. We shall then examine the degree of applicability of these equations to our system.

Derivation of the Kinetic Equations.—Protonation of the alcohol R_2CHOH is expected to convert it into a species relatively or totally unreactive in hydride transfer to a carbonium ion, for the direct product of hydride loss from such a species would have positive charges on adjacent atoms and none of the stabilization which helps to drive the reaction. Therefore we write

$$\frac{-d[(T^+) + (TOH)]}{dt} = k_2^0(T^+)(R_2CHOH) \quad (1)$$

for the rate of disappearance of the color of the carbonium ion T^+. Treating the aliphatic alcohol as a simple base, we write

$$\frac{[R_2CHOH][H^+]}{[R_2CHOH_2^+]} = K_A = \frac{(R_2CHOH)h_0}{(R_2CHOH_2^+)} \qquad (2)$$

where $h_0 = [H^+]\,(f_B/f_{BH^+})$. Parentheses here denote concentrations, square brackets activities, and f's activity coefficients. Equation 2 enables us to establish a relation between the unchanging constant k_2^0 of equation 1 and the corrected observed rate constant k_2 (referred to 100% T^+) in a series of solutions.

Total alcohol = a = $(R_2CHOH) + (R_2CHOH_2^+)$

$$a = (R_2CHOH)(1 + (h_0/K_A)) \qquad (3)$$

whence

$$(R_2CHOH) = aK_A/(h_0 + K_A) \qquad (4)$$

Substituting 4 into 1

$$\frac{-\mathrm{d}\,(T^+) + (TOH)]}{\mathrm{d}t} = k_2^0(T^+)a\,\frac{K_A}{h_0 + K_A} \qquad (5)$$

It follows that

$$k_2 = k_2^0\,K_A/(h_0 + K_A) \qquad (6)$$

or

$$k_2h_0 = k_2^0K_A - k_2K_A \qquad (7)$$

Analysis of the Rate Data.—By the use of equation 7 it is possible in principle to determine, from a set of measurements of k_2 over a range of acidity values, both the basicity constant of the alcohol, as expressed by K_A for its conjugate acid, and the limiting value k_2^0 for the bimolecular rate constant for reaction between the carbonium ion T^+ and the uncharged basic form of the alcohol. Such a determination can succeed in fact only when the measurements extend into that region of acidity where some reasonable fraction, say between 20 and 80%, of the alcohol is converted into its oxonium ion. If the measurements are restricted to more acid media than this, then the quantity h_0k_2 will be practically constant and, although a value of the intercept, $k_2^0K_A$, can be estimated it will not be possible to resolve this into its factors. Any uncertainty in the effective acidity functions of the solutions will result in a distortion in the values entering into equation 7. This situation is illustrated by the data for the reaction of triphenylcarbinol with isopropyl alcohol. The rate of disappearance of carbonium ion was measured with five different concentrations of isopropyl alcohol in three different sulfuric acid–water mixtures, and four alcohol concentrations in a fourth sulfuric acid–water mixture, nineteen rate measurements in all. The data obtained at the highest alcohol concentration, 0.621 M, fail completely to fit equation 7, showing values of h_0k_2 which alternately increase and decrease with rising k_2. The data for the lower alcohol concentrations, 0.129 and 0.256 M, fall upon a common line. The points for alcohol concentrations of 0.380 and 0.501 are rougher, but all the points up to $k_2 = 6 \times 10^{-4}$ are consistent with a value of $pK_A = -3.2 \pm 0.2$ and $k_2^0 = 2 \times 10^{-3}$. These data are plotted in Fig. 3.

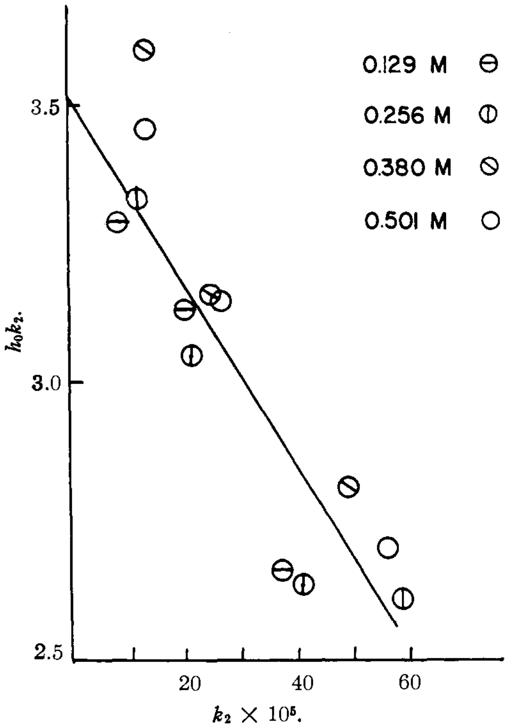

Fig. 3.—Application of equation 7 to kinetic data for reaction of triphenylcarbonium ion with isopropyl alcohol at concentrations up to 0.501 M.

The seven determinations of the rate of disappearance of the dianisylcarbonium ion in the presence of isopropyl alcohol were all made at alcohol concentrations of 0.502 M. Because this carbinol gives good carbonium ion concentrations at lower acidities than does triphenylcarbinol, the measurements extend into a region where there is more free isopropyl alcohol and the values of k_2h_0 vary over a threefold range. As shown in Fig. 4 six of these points fall on a satisfactory straight line, the only exception being a run at H_0 −4.07, which showed an unaccountable acceleration late in its

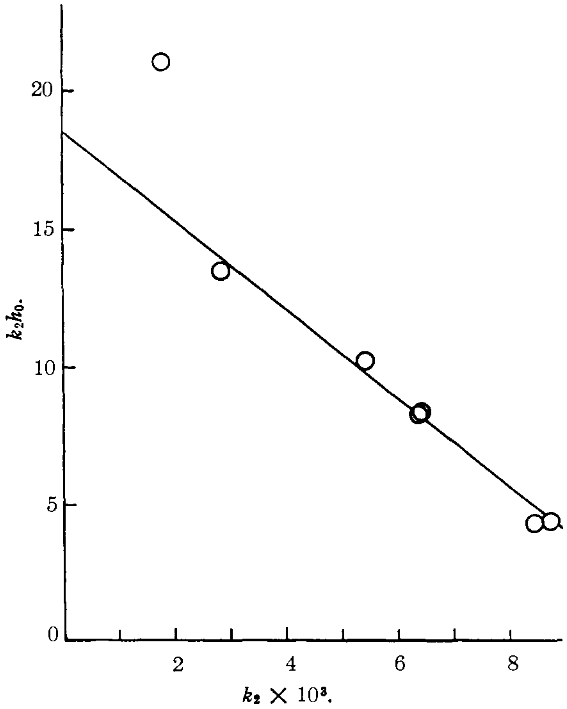

Fig. 4.—Application of equation 7 to kinetic data for reaction of dianisylcarbonium ion with isopropyl alcohol at concentrations of 0.501 M.

course. The line gives pK_A -3.2 in complete agreement with the determination using triphenylcarbinol, and $k_2^0 = 1.2 \times 10^{-2}$.

It may be concluded that additions of more than 0.5 M isopropyl alcohol invalidate the use of a common H_0 function for indicators, arylcarbinols and alcohols, or so disturb the activity of water that the parallel between H_0 and C_0 is seriously upset. At the same time it is clear that if the additions of alcohol to the sulfuric acid–water mixtures are kept as small as possible the expected dependence of rate on acidity function is observed and a valid way is at hand of determining the basicity of a simple alcohol. It is evident also that the experience gained in this study should enable us to choose conditions for much more accurate measurements of this sort, and we are engaged in the performance of such measurements.

Effect of Structure upon Over-all Rate Constant.—Included in Table II are the bimolecular rate constants of hydride transfer to triphenylcarbonium ion by a series of alcohols, expressed as the product $k_2^0K_A$, which can in each case be determined with some assurance by the treatment just outlined. We shall not report the pK_A values of the alcohols other than isopropyl at this time, pending more accurate evaluation. The differences among the constants of Table II depend in part upon the differing basicities of the alcohols and in part upon their reactivities as hydride donors.

TABLE II

HYDRIDE TRANSFER FROM ALCOHOLS AND ETHERS TO TRIPHENYLCARBONIUM ION AT 25°

Alcohol	Mole/l.	H_0	$k_2 \times 10^5$ l./mole sec.	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, cal./deg. mole	Estd. $k_2^0K_A$
Ethyl	0.652	−3.74	5.6	16.8	−22	0.3
n-Propyl	.503	−3.68	4.3	17.5	−20	.2
i-Butyl	.421	−3.73	0.58	17.9	−23	.04
i-Propyl	.501	−3.68	56.5	14.3	−26	3.5
s-Butyl	.414	−3.72	27.4	14.5	−26	2.4
α-Methylisobutyl	.353	−3.52	6.4	..	..	0.3
Pinacolyl	.154	−3.70	2.2	..	..	.2
Ether						
Diethyl	.369	−3.75	5.5	18.9	−15	.6
Diisopropyl	.272	−3.80	14.0	16.8	−21	1.3

The Low Basicity of Isopropyl Alcohol.—In the case of isopropyl alcohol enough information is at hand to show clearly that the isopropyl group, substituted for hydrogen in water, has a substantial base-weakening effect upon the oxygen atom. This is the opposite of what would be expected on strictly electrochemical grounds, and corresponds to the extreme reversal envisaged by Brown for the successive substitution into ammonia of an alkyl group so bulky as to make "B-strain" completely dominant.[26] We recognize two factors which might make oxygen compounds more sensitive to B-strain than amines. (It seems unlikely that solvation forces would respond so differently to bulk in the two series.) The first factor is the slightly smaller covalent radius of oxygen, 0.66 compared to 0.70 for nitrogen.[27] That the phenomena attributable to B-strain are sensitive to the covalent radius of the central atom is already indicated by the relative stability of tri-*t*-butylboron–ammonia,[28] tri-*t*-butylamine being unknown, (covalent radius of boron, 0.88) and the "normal" order of basicity in the alkylphosphines (covalent radius of phosphorus, 1.10).[29] Even so, the idea that B-strain should be dominant even in monosubstitution on oxygen at the tetrahedral angle seems to place rather a burden upon the steric requirement of the proton.

The second factor in the difference between the oxygen and nitrogen series may well be much more important. An ammonium ion, involving quadricovalent nitrogen, obviously must have equivalent sp^3 hybrid orbitals like those of methane. However, in an oxonium ion only three orbitals are involved in bonding and the fourth holds an unshared electron pair. The view[30] that a prohibitive promotional energy would be involved in the allocation of the 2s orbital of oxygen to any use other than the accommodation of the unshared pair suggests a very simple picture of oxonium ion formation according to which B-strain would necessarily be a dominant factor. Let us suppose that water, alcohols, ethers and oxonium ions all have only p orbitals occupied in bond formation. Then the preferred bond angle is 90°, which is unattainable on steric grounds even for water. The strain in an alcohol, ether or oxonium ion increases steadily with each group introduced and with every increment in the steric requirement of such groups; and even when the bond angle in an ether exceeds that normal for tetrahedral hybridization, the bonding orbitals remain essentially *p* orbitals under substantial strain. This strain will, of course, always be more intense with the multiple interaction of groups in an oxonium ion than in the initial alcohol or ether, and will always operate accordingly to lower the basicity.

Effect of Alcohol Structure on the Rate of Hydride Transfer.—The quantity $k_2^0K_A$, recorded in Table II, will be determined by the summation of three major effects. This rate quantity will be larger, (1) the lower the basicity of the alcohol concerned, (2) the more stable the protonated ketone resulting from hydride loss, and (3) the less hindered the access to the α-hydrogen atom which is to be transferred as a hydride ion. Of these three factors, accumulation of alkyl groups in a primary or secondary alcohol should favor hydride transfer through the first and second factors, and hinder it through the third. Thus the range of rates shown by this measure of reactivity is not as wide as we should expect on determination of the quantity k_2^0 itself. The table shows that the secondary alcohols have in general higher values of $k_2^0K_A$ than the primary alcohols, but that in each series the reactivity decreases with increasing branching of the alkyl chain. It follows that within the series of primary or the series of secondary alcohols, changes in structure affect the rate of hy-

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[26] H. C. Brown and H. Pearsall, THIS JOURNAL, **67**, 1766 (1945).

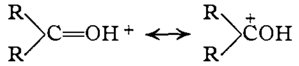
[27] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., Second Edition, 1945, p. 164.

[28] H. C. Brown, THIS JOURNAL, **67**, 377 (1945).

[29] H. C. Brown, *ibid.*, **67**, 503 (1945).

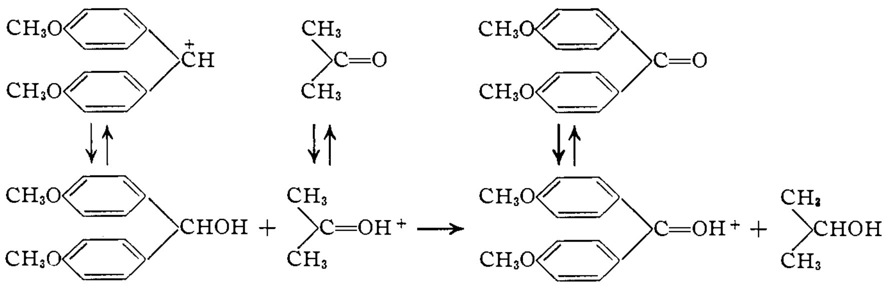
[30] Pauling, ref. 27.

dride transfer more through steric hindrance at the α-hydrogen atom than by changes in the basicity of the alcohol plus changes in the inherent ease of hydride removal. This is entirely reasonable in view of the large steric requirement of the triphenylcarbonium ion. The non-reactivity of methanol, and the generally greater reactivity of secondary as compared to primary alcohols, may then be attributed to basicity effects on the alcohols and ketones in some as yet unknown proportion. It will be noted that neither of the reasons why alkyl substitution might depress the basicity of an alcohol can apply to a ketone or aldehyde; the carbonyl atom is bonded by sp^2 orbitals with ample bond angles in both the protonated and unprotonated state, and the change from formaldehyde to a larger aldehyde and then to a ketone must be accompanied by the full inductive and hyperconjugative stabilization which the alkyl groups can impart to the ion



which is the direct product of hydride transfer from the corresponding alcohol. Thus we may well have the paradoxical situation that alkyl substitution which makes the original alcohol a weaker base makes the ketone or aldehyde related to it a stronger base and thus doubly favors hydride transfer from the alcohol.

Effect of Temperature.—Table II shows the enthalpy and entropy of activation for the reaction of five alcohols and two ethers with triphenylcarbonium ion. These quantities are, of course, composite and include any change in K_A with temperature as well as changes in the rate constant for hydride transfer by the neutral alcohol. In view of this we can assign little significance to the differences in the series. We note, however, that the substantial negative entropy of activation common to all the alcohols and ethers is consistent with the crowded and highly oriented nature of the transition state which must be involved in the direct transfer of H$^-$ from an alcohol or ether to a tertiary carbonium ion.

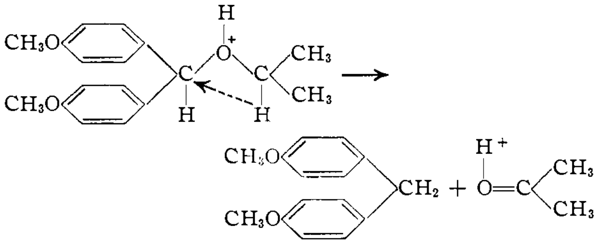


Effect of Carbonium Ion Type.—Other factors being constant, the more stable carbonium ions would be expected to be the less reactive in hydride capture. This is borne out in an experiment with tri-*p*-anisylcarbinol,[31] which was found to have an ionization constant larger by 7.36 logarithmic units than that of triphenylcarbinol. This stable carbonium ion was quite unreactive in hydride transfer with isopropyl alcohol, being only 1/1000 as fast as the triphenylcarbonium ion.

Comparison of dianisylcarbinol with triphenylcarbinol presents a different situation. The value of k_2^0 for dianisylcarbonium ion is 6 times greater than for the triphenyl although the ionization constant for the former is about 8 times the greater, indicating a better stabilized carbonium ion. The explanation lies in the different steric requirements for these two reactants. The activation energy for dianisylcarbinol is indeed about 0.5 kcal. greater, but the activation entropy is 6 e.u. less negative, corresponding to the considerably smaller congestion in the transition state.

The Reaction of Dianisylcarbinol with Acetone.—Acetone was shown to be inert toward triphenylcarbonium ion under the conditions of the present reaction (Fig. 1). Dianisylcarbinol, however, is decolorized at H_0 −3.20 at a first-order rate which is proportional in different runs to the concentration of acetone present. Dianisyl ketone was recognized in the product by its spectrum in concentrated sulfuric acid, λ_{max} 405 mμ, ϵ 3880. In less acid solutions the rate falls off much more rapidly than in the similar reaction with alcohols as hydride donors. This reaction is evidently the cationic counterpart of the anionic carbinol–carbonyl interconversions realized in strongly basic media by Doering and co-workers, and of the concerted Meerwein–Ponndorf–Verley–Oppenauer interconversions occurring in the neutral molecules. The reacting form of the dianisylcarbinol is not the carbonium ion but the neutral alcohol in equilibrium with it, which is acting as hydride donor to the conjugate acid of acetone. The fraction of dianisylcarbinol in this neutral form should be 0.070 at H_0 −3.30. With the limited basicity of acetone (pK_A −3.7)[32] the fraction present as oxonium ion at H_0 −3.30 is 0.29 and the corresponding k_2^0 is $(1.35 \times 10^{-3})/(0.07 \times 0.29) = 0.066$. Thus the range of conditions for hydride transfers between alcohols and ketones is complete, extending from the most basic conditions to the most acidic.

1,1-Dianisyltetrahydrofuran.—Because of the rapid equilibration of the arylcarbinols and alcohols with the corresponding mixed ethers, the kinetic data cannot exclude the possibility that the actual hydride transfer which is preferred in these systems is an intramolecular one between the two α-positions of the mixed ether ion



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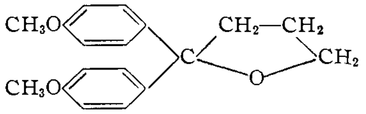
[31] Deno, Jaruzelski and Schriesheim, ref. 22.

[32] W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **8**, 175 (1940).

The only factor which might make such a roundabout path favorable would be the sterically hindered nature of the reactants and the high orientation required for the direct hydride transfer. We prepared 1,1-dianisyltetrahydrofuran (I) with the thought that in this case the orientation requirement for the requisite hydride transfer would be considerably more severe in the ether or its oxonium ion than in the acyclic δ-hydroxypropyldianisylcarbonium ion (II) in equilibrium with it. In the event that the direct transfer should be somehow unfavored, this compound would appear unreactive under our reaction conditions. There are a number of reasons why this test of mechanism is not a conclusive one. The compound, however, appeared reactive, with a first-order rate constant, based upon the disappearance of absorption at 390 mμ, of 1.22×10^{-4} sec.$^{-1}$, entirely consistent with the picture of direct hydride transfer developed above.



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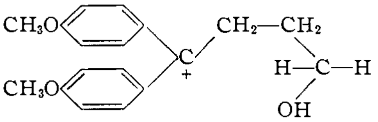
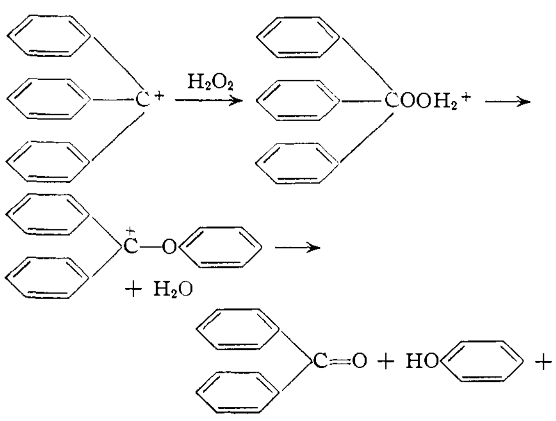


II

The Reaction of Arylcarbonium Ions with Peroxides.—A considerable number of runs were made with the triphenylcarbinol–isopropyl alcohol system before certain inconsistencies in the data suggested the presence of an impurity in some carefully distilled isopropyl alcohol which had been standing for some time before use. At length the alcohol was found to give a positive peroxide test with the thiocyanate–ferrous reagent and an iodometric analysis for 0.08 mole per cent. peroxide. No other of our alcohol samples ever showed peroxide, although it was possible to build up a peroxide titer in isopropyl alcohol by bubbling air through it in the presence of cupric oxide. The ethers needed very careful purification to free them of peroxide, and they were always freshly distilled immediately before use. When this did not completely free them of peroxide, it reduced the amount sufficiently to show a break from fast to slow reaction as the peroxide was rapidly consumed.

The presence of 2.34×10^{-4} M hydrogen peroxide (the concentration of the impurity in the runs with impure alcohol) at H_0 -3.80 caused the color of triphenylcarbonium ion to disappear with a first-order rate constant of 4.35×10^{-4} sec.$^{-1}$, much faster than the rate due to alcohol alone. Benzophenone and phenol were detected as products, showing that the reaction is the rearrangement of Wieland and Maier[33,34]

This rapid reaction is a sensitive, though not specific, test for peroxides, as well as a powerful method of degrading tertiary alcohols.



Kinetic Isotope Effect.—Measurements of the rate of reduction of triphenylcarbinol by isopropyl alcohol labeled and unlabeled with deuterium at the α-position showed a ratio $k_H/k_D = 2.58$, in poor agreement with the ratio of 1.84 deduced from the deuterium analyses of alcohol and triphenylmethane. We place more reliance on the latter value as being based upon competition between isotopic atoms present in one and the same environment.

Experimental

Disproportionation of Dianisylcarbinol in Trichloroacetic Acid-*d*.—Trichloroacetic acid-*d* was made by the reaction of trichloroacetic anhydride (prepared by the method of Swarts)[35] with deuterium oxide $d^{20}{}_4$ 1.10514, from Norsk Hydro-Elektrisk Kvaelstofaktieselskab, in a 1:1 molar ratio (5.7 g. of the anhydride and 0.38 g. of D_2O) in a glass tube arranged for continuous sweeping with dry nitrogen. The acid obtained melted at 1.1°.

Di-*p*-anisylcarbinol, m.p. 70–71°, recrystallized from methanol, was prepared by reduction of Eastman Kodak Co. White Label di-*p*-anisyl ketone, m.p. 143–144°, with lithium aluminum hydride. The carbinol (1.14 g., 0.005 mole) was mixed with 0.4 g. of trichloroacetic acid-*d* in a tube kept under dry nitrogen and held at 40° for six hours. The mixture was then dissolved in benzene and extracted with 10% aqueous potassium carbonate solution, dried and evaporated. Following the procedure of Balfe, Kenyon and Thain, the mixture was triturated with petroleum ether (b.p. 30–60°). The suspension was filtered, the filtrate concentrated and cooled to give 0.34 g. of dianisylmethane, m.p. 46–47°. This product was subjected to combustion and the product water analyzed densitometrically by the method of Anfinsen.[36] The gradient density tube used was prepared by Dr. V. J. Shiner in these laboratories and the analysis was kindly made for us by Mr. R. P. Anderson. The product water was indistinguishable from the standard sample of deuterium-free water. The infrared spectrum of the di-*p*-anisylmethane in the CD stretching region was identical with that of the reference material prepared by Clemmensen reduction from the ketone.

Products of the Reaction between Triphenylcarbinol and Isopropyl Alcohol.—A solution of 1 g., 0.0038 mole, of triphenylcarbinol in 10 ml. of concentrated sulfuric acid was carefully diluted with 3.5 ml. of water and 6.25 g., 0.104 mole, of isopropyl alcohol was added. Within five minutes a precipitation of white needles commenced. The solution was agitated for four hours and the reaction quenched by pouring into an excess (10 ml.) of water. The white crystalline mass was filtered in a sintered glass crucible, washed thoroughly and dried to give 0.95 g. (0.0038 mole) of product. After recrystallization from cyclohexane the product melted at 91–91.5°, undepressed with authentic triphenylmethane.

The acid filtrate plus the first washings of the precipitate was treated with 2,4-dinitrophenylhydrazine. The light

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(33) H. Wieland and J. Maier, *Ber.*, **64**, 1205 (1931).

(34) See M. S. Kharasch, A. Fono, W. Nudenberg and A. C. Poshkus, *J. Org. Chem.*, **15**, 775 (1950).

(35) F. Swarts, *Bull. soc. chim. France*, [3] **13**, 992 (1895).

(36) C. Anfinsen in "Preparation and Measurement of Isotopic Tracers," D. W. Wilson, A. O. C. Nier and S. P. Reimann, J. W. Edwards, Ann Arbor, Mich., 1946, p. 61.

yellow crystals which formed were recovered by filtration and dried to a weight of 0.56 g. (0.0024 mole, 63%). After recrystallization from ethanol the product melted at 125–126° undepressed on admixture with the authentic hydrazone from acetone.

The Reaction of Triphenylcarbinol with α-Deuterioisopropyl Alcohol.—α-Deuterioisopropyl alcohol was prepared by the reduction of acetone with lithium aluminum deuteride. The deuteride, 1.00 g. (0.095 equivalents), was suspended in 50 ml. of anhydrous ether in a flask cooled in ice. Analytical reagent acetone, 6.0 g. (0.099 mole), was added slowly with agitation. A vigorous reaction ensued. Following the addition of acetone the flask was allowed to stand at room temperature for four hours. Ethylene glycol, 8.0 ml., was added slowly to the mixture to destroy unreacted lithium aluminum deuteride. The products were fractionally distilled from the reaction flask through an 85-cm. glass helix packed column. The fraction boiling at 80–82°, 5.3 g. (0.087 mole), was taken as the deuterated alcohol, $n^{20}\mathrm{D}$ 1.3772. By combustion and densitometric analysis this alcohol was found to contain 0.874 atom of deuterium per molecule, the analysis being performed by Mr. R. P. Anderson.

Triphenylcarbinol, 1.00 g. (0.0038 mole) was dissolved in 5 ml. of concentrated sulfuric acid. The solution was diluted with 2.5 ml. of water and 1.25 g. (0.039 mole) of 2-propanol-2*d* was added. The mixture was stored overnight, quenched and worked up as before. Triphenylmethane, m.p. 91–92°, was obtained in 98% yield. The infrared spectrum showed a band at 4.78 μ attributable to the CD vibrational frequency. Combustion and analysis of the product water in a gradient density apparatus by Mr. Anderson showed the product to contain 4.99 atom per cent. deuterium, corresponding to 0.798 atom of D per molecule.

Preparation of 1,1-Di-*p*-anisyltetrahydrofuran.—By analogy with the diphenyl derivative[37] this compound was prepared from the reaction of the *p*-anisyl Grignard reagent with γ-butyrolactone. *p*-Anisylmagnesium bromide was prepared from 20 g. (0.106 mole) of anisyl bromide and 2.7 g. of magnesium chips in dry ether. After the addition of 3.9 g. (0.045 mole) of γ-butyrolactone a pasty complex was formed. The mixture was heated under reflux for two hours, cooled and hydrolyzed with a saturated aqueous ammonium chloride solution. The product was taken up in benzene, the benzene dried and evaporated and the resulting hard crystalline mass was dissolved in boiling cyclohexane (60 ml.) and subjected to chromatography through 100 g. of alumina. Benzene eluted a waxy solid, 6.8 g., m.p. 62–63° after recrystallization from cyclohexane. The infrared spectrum indicated the absence of hydroxyl groups. Bands were present characteristic of the dianisyl system (6.1, 6.5 doublet, 6.65, 6.83, 8.0, 9.7). Recrystallization from cyclohexane yielded a material melting constantly at 62.7–63.0°. In sulfuric acid the material gave a red coloration, λ_{max} 495 mμ, in the region characteristic of the dianisylcarbonium ion.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.10. Found: C, 75.72; H, 6.97.

The Reaction of Triphenylcarbinol with Hydrogen Peroxide.—The yellow color of a solution of 1 g. of triphenylcarbinol in 5 ml. of concentrated sulfuric acid with 5 ml. of water was discharged within one minute by the addition of 10 ml. of 3% aqueous hydrogen peroxide followed by vigorous agitation. Following alkaline extraction there was isolated 0.55 g. of benzophenone, m.p. 46–47°, and, after bromination, 0.11 g. of 2,4,6-tribromophenol, m.p. 91–93°.

Measurements.—The spectroscopic measurements were made on a Coleman junior grating spectrophotometer when only work in the visible region was involved and on a Beckman DU quartz prism spectrophotometer otherwise. Since the Coleman instrument has a band width of 35 mμ, offering the possibility of mechanical deviations from Beer's law at moderate and high absorbancies, the applicability of Beer's law was checked empirically for each colored substance which was to be measured on the Coleman instrument.

Preparation of Indicators.—The solutions used in this study fell within the span of two of the indicators used by Hammett and Paul,[38] namely, 2,4-dinitroaniline, pK_A −4.38, and 2,4-dichloro-6-nitroaniline, pK_A −3.22. The sample of the former indicator used was Eastman Kodak Co. White Label material recrystallized to a constant spectrum.

The second indicator, 2,4-dichloro-6-nitroaniline, was prepared by the chlorination of 2-nitro-4-chloroaniline by an adaptation of a method described by Hickinbottom for the chlorination of *o*-bromoaniline.[39] A 10-g. sample of 2-nitro-4-chloroaniline, obtained from the Eastman Kodak Co., was dissolved in 400 ml. of 25% aqueous hydrochloric acid. Chlorine was bubbled through the solution. The chlorinated product was only slightly soluble in this acid and precipitated as the reaction proceeded. The product was filtered off and the filtrate again treated with chlorine. After about three hours the further passage of chlorine produced only a slight precipitation. The spectrum of the product was constant after four recrystallizations from ethanol. The final yield was 8.1 g. of light yellow product, m.p. 101.8–102.2°.

Evaluation of the ionization ratios was accomplished essentially by the methods of Hammett. In several cases the measurements were made both with the Beckman and with the Coleman instruments and it was verified that identical results were obtained. Following a procedure of Gold and Hawes, designed to correct for any shift of maximum with solvent, the extinctions were measured at 340 and 348 mμ in the case of 2,4-dinitroaniline. The corrected results did not differ significantly from the uncorrected values using a single wave length. Consequently the remainder of the solvent ratios were calculated without this procedure.

A range of stock sulfuric acid–water solutions from 22–75% sulfuric acid was prepared by dilution by weight of concentrated sulfuric acid with distilled water. The concentrations were determined both by specific gravity and by dilution followed by titration with standard base.

The kinetic technique involved the addition of various alcohols to aliquots of the above stock solutions. The acidities at which the runs were actually made, therefore, did not correspond to the acid concentrations of the stock solutions but were somewhat more dilute. To determine the H_0 at which each run was made, an experiment with indicator in place of the arylcarbinol substrate but otherwise identical with the rate runs was set up for each of the rate measurements made. The procedure involved the addition of 0.030 ml. of the indicator as a standard solution in methanol to 5.00 ml. of a given stock acid solution in a glass-stoppered Corex cell. The necessary volume of the alcohol used as a reductant in the kinetic runs was then added. The tube was shaken vigorously to mix the contents and brought to 25°. Finally, the absorbancy of the solution was determined in the spectrophotometer. As indicated, concentrations were measured volumetrically at 25°. For measurement of volumes less than 0.2 ml., graduated sereological pipets were used. All pipets were calibrated at 25°.

Measurements of Rates and Equilibria.—Temperature control at 25.05 ± 0.01° was accomplished with a variably heated, constantly cooled, bath controlled by a toluene–

TABLE III

REACTION BETWEEN DIANISYLCARBINOL AND ISOPROPYL ALCOHOL IN SULFURIC ACID–WATER SOLUTION AT 25.05°

Dianisylcarbinol, 2.52 × 10^{-5} *M*; isopropyl alcohol, 0.501 *M*; H_0 − 3.11

Time, min.	A_s
0	0.341
3.10	.235
3.84	.212
4.50	.196
5.45	.178
6.20	.162
7.40	.139
8.85	.121
11.60	.093
∞	.058

$k_1 = 2.95 \times 10^{-3}$ sec.$^{-1}$

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[37] C. Weizmann and F. Bergmann, THIS JOURNAL, **60**, 2647 (1938).

[38] L. P. Hammett and M. A. Paul, *ibid.*, **56**, 827 (1934).

[39] W. J. Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Co., London, 1948, 2nd ed., p. 322.

mercury thermostat regulator. The reaction tubes were inserted in the bath and removed at intervals for measurement in the colorimeter. The intermittent withdrawal of the tubes introduced no detectable error since the interval between measurements was of long duration compared with the ten seconds required to obtain the color measurement.

For elevated temperatures the runs were made in cells immersed in solvent boilers. Acetone and benzene were used to give temperatures of 57 and 80°, respectively, in the boilers.

Because of the presence of the alcohol in enormous excess over the carbonium ion the rates were generally susceptible to treatment as first-order reactions. The specific rate constants were evaluated from the equation

$$2.303 \log_{10} \frac{A_{si} - A_{s\infty}}{A_s - A_{s\infty}} = k_1 t$$

where A_{si} represents initial absorbancy; A_s, the absorbancy at time t; $A_{s\infty}$, the absorbancy at infinite time; t, the time in seconds; and k_1, the specific rate in sec.$^{-1}$. The slope of a plot of log $(A_{si} - A_{s\infty})/(A_s - A_{s\infty})$ against t was used to determine k_1.

Table III gives a set of representative data for the reduction of dianisylcarbinol by isopropyl alcohol.

Acknowledgment.—The expenses of this research were met by a grant from the Mallinckrodt Chemical Works.

CAMBRIDGE 38, MASS.

[CONTRIBUTION FROM THE TEXTILE FIBERS DEPARTMENT, PIONEERING RESEARCH DIVISION, E. I. DU PONT DE NEMOURS AND CO., INC.]

Kinetics of Reactions of Acyl Chlorides. II. Mechanisms of Hydrolysis of Sulfonyl Chlorides

BY H. K. HALL, JR.

RECEIVED AUGUST 10, 1955

The hydrolysis and amidation rates of a series of sulfonyl chlorides, ZSO_2Cl, [Z = CH_3–, C_6H_5–, CH_3O–, C_2H_5O– and $(CH_3)_2N$–] were determined. Methane- and benzenesulfonyl chlorides hydrolyzed by an SN2 mechanism, whereas dimethylsulfamyl chloride underwent ionization (SN1). The alkoxysulfonyl chlorides underwent ionization at the S–Cl bond, followed by rapid nucleophilic attack on carbon, but some contribution of bimolecular reactions could be detected.

The kinetics of hydrolysis of sulfonyl chlorides, ZSO_2Cl, where Z may be CH_3–, C_6H_5–, CH_3O– or $(CH_3)_2N$–, has been studied by relatively few investigators. The classical investigation of Berger and Olivier,[1] relating to the hydrolysis of aromatic sulfonyl chlorides in aqueous acetone, was extended by the very careful measurements of Hedlund[2] to pure water solutions. The latter investigator also studied alkanesulfonyl chlorides, showing that these compounds hydrolyze much more slowly than the aromatic derivatives. More recently Swain and Scott[3] have shown that benzenesulfonyl chloride in aqueous acetone is highly susceptible to nucleophilic attack by hydroxyl ion or aniline. Linetskaya and Sapoznikhova have supplied additional data on hydrolysis rates of aromatic sulfonyl chlorides.[4] Böhme and Schürhoff,[5] working in aqueous solutions of water-soluble ethers, confirmed that methanesulfonyl chloride hydrolyzes very slowly, but noted that it was very reactive toward methoxide ion.

No kinetics studies have yet been made of the hydrolysis of an alkoxysulfonyl chloride (alkyl chlorosulfonate) or of a sulfamyl chloride. As a continuation of our studies of displacement reactions on carbonyl chlorides,[6] it was of interest to investigate the mechanisms of reaction available to these two types of sulfonyl halide.

Experimental

Materials.—The following compounds were purchased from Eastman Kodak and were redistilled: methanesulfonyl chloride, b.p. 31° (1 mm.), $n^{20}D$ 1.4509; benzenesulfonyl chloride, b.p. 117.5° (12 mm.); ethyl chlorosulfonate, b.p. 30° (1 mm.), $n^{20}D$ 1.4155. Dimethylsulfamyl chloride was prepared by refluxing 100 g. of dimethylamine hydrochloride (Eastman Kodak Co.) with 512 g. of sulfuryl chloride (Hooker Electrochemical Co.) overnight and distilling the reaction mixture directly.[7] There was obtained 120.4 g. of product, b.p. 67° (8 mm.) (lit.[13] b.p. 66° (10 mm.)), $n^{20}D$ 1.4524 (lit.[13] $n^{20}D$ 1.4526). Methyl chlorosulfonate, b.p. 36° (12 mm.) (lit.[8] b.p. 48.1° (29 mm.)), $n^{20}D$ 1.4128–38 (lit.[8] $n^{20}D$ 1.414), was prepared by the reaction of methanol with sulfuryl chloride.[8]

Solvents.—It was noted that solutions of ethyl chlorosulfonate in reagent grade acetone rapidly turned a deep red color. Accordingly, the kinetic runs were made in aqueous dioxane instead of aqueous acetone. Dioxane was purified by the method of Fieser.[9] The mixed solvents were made up by volume at 25.0°.

Kinetics Methods.—The methods of following the rates already have been described.[6] It was found for ethyl chlorosulfonate and dimethylsulfamyl chloride that the rate constants in pure water lacked precision and gave unsatisfactory Arrhenius plots. Subsequent measurements were made in 86.1% water–13.9% dioxane. Under these conditions dimethylsulfamyl chloride behaved satisfactorily, but the data for ethyl chlorosulfonate were still unsatisfactory. Attention was diverted to the more hydrophilic methyl chlorosulfonate, and this chloride in the mixed solvent gave better data. Representative rate plots are given in Fig. 1 and the Arrhenius plots are shown in Fig. 2.

One additional kinetics method was devised in order to obtain data for alkaline and aminiacal solutions in which the silver–silver chloride electrodes did not behave satisfactorily. This consisted of hydrolyzing the acid chloride in the presence of one-half an equivalent of alkali or amine. The pH of the reaction solution was noted as a function of time. The time at which the solution changed from alkaline to acidic was sharply defined and was taken as the half-life of the reaction, from which k_1 could be calculated. By this "half-life" method, it was confirmed that the rate of hydrolysis of dimethylcarbamyl chloride, which was studied earlier,[6] was unaffected by added amines or alkali.

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