20 hours; esters 1,2,5,7,8,10,12,15,17 of Table I. (2) (a) Potassium cyanide, sulfonic acid ester dissolved in hot 95% ethanol, cyanide dissolved in 60% ethanol, refluxed for 12 hours; esters 1,2,5,7,8,10,11,12,15,16,17. (b) Cuprous cyanide, anhydrous pyridine, refluxed for 40 hours, ester 10. (3) Benzylmagnesium chloride, absolute ether, refluxed for 8 hours and allowed to stand for 16 hours; esters 1,2,5,6, 7,8,10,12,16,17. (4) Benzylmagnesium chloride; *n*-butyl ether; refluxed for 8 hours; ester 8. (5) 2-Aminopyridine; benzene; refluxed for 48 hours or allowed to stand for 30 days at room temperature; ester 8.

The working-up of the reaction mixtures was carried out in straightforward fashion and offered no difficulties. Small amounts of tarry residues were not further investigated.

The alkylations were uniformly unsuccessful, the yield of recovered ester being usually about 90% where there was no reaction at all. In other cases, decomposition of the sulfonates occurred. The recovery of unreacted ester and decomposition products frequently accounted for about 80% of the starting material.

In reaction (2), several variations in conditions were imposed, *e.g.*, heating of the sulfonate with solid potassium cyanide or in pyridine with cuprous cyanide, or using aqueous Carbitol rather than aqueous ethanol as the solvent, with no greater success. In fact, when the tosylate was heated with a mixture of solid potassium cyanide and sodium iodide, in the hope that the iodide might catalyze the displacement, a small amount of the iodonitroalkane was apparently formed instead of the desired nitrile.

In several instances it was noticed that ammonia was given off while the esters were refluxed with potassium cyanide (especially in the cases of the high-temperature reactions using aqueous Carbitol as a solvent, but also in the cases of the *p*-bromobenzenesulfonate and the 3,4-dichlorobenzenesulfonate, where aqueous ethanol was the solvent). Since there was the possibility that a nitrile was being formed and then hydrolyzed to the potassium salt of β-nitro-β-methylbutyric acid and ammonia, an attempt was made to isolate this acid in the case of the *p*-bromo and the 3,4-dichloro esters. For example, the basic aqueous solution, which remained after removal of the alcohol and of the sulfonic acid ester and other ether-soluble non-acidic organic materials, and which would contain any acid, was acidified with dilute hydrochloric acid; but the expected evolution of hydrogen cyanide was not observed. The solution was then extracted with ether; the ether extract was dried over magnesium sulfate; and the ether was removed under vacuum. Two substances were obtained from the green ether solution: an oil, and a white solid with a pungent odor. The two were separated by filtration. Distillation of the oil gave mainly one substance, an acidic liquid, b.p. 105°, which did not contain nitrogen, and which presumably was formic acid. The white solid was quite soluble in most organic solvents, giving an intense blue solution in each case. It was found to contain nitrogen, and after recrystallization from chloroform it melted at 74–75° to give a blue liquid that decomposed immediately. The blue color of the solutions and of the pure liquid indicated that the substance was a nitroso compound, and probably the pseudonitrole, $(CH_3)_2C(NO_2)NO$, which has a melting point of 76°. A mixed melting point of an authentic specimen (prepared by acidification by dilute hydrochloric acid of a solution of sodium nitrite and 2-nitropropane in dilute sodium hydroxide) with the material from the cyanide reaction showed no depression. Evidently 2-nitropropane and nitrogen oxides were formed by the decomposition of the sulfonates.

The amount of ester that was recovered in the attempted alkylation of potassium cyanide with the *p*-bromobenzenesulfonate in aqueous ethanol was 55%. The pseudonitrole which was obtained accounted for an additional 20% (0.01 mole of the pseudo-nitrole was obtained when 0.1 mole of the ester was used). The remaining 25% was not accounted for, but may have given additional amounts of nitrogen oxides as decomposition products, and thus would not be isolated.

Oxides of nitrogen were observed in reaction (4); in reaction (2) if Carbitol was the solvent; and in reaction (5) if nitrobenzene was used in place of benzene as the solvent. The ester of 3,4-dichlorobenzenesulfonic acid (Table I, ester 8) was selected for reactions (4) and (5) because it had given the highest yield in the reaction with sodium iodide in acetone. Appreciable amounts of toluene and bibenzyl were isolated from reactions (3) and (4).

NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Reaction Rates by Distillation. V. The Effect of Changes in Structure on the Basicity of Selected Ketones, Esters, Ethers and Alcohols[1]

BY ERNEST F. PRATT AND KEN MATSUDA[2]

RECEIVED MARCH 26, 1953

The relative basicities of sixty-one selected ketones, esters, ethers and alcohols have been quantitatively determined by measuring their ability to decrease the rate of the acid-catalyzed self-etherification of benzhydrol or the dehydration of *t*-butyl alcohol in benzene solution. The major conclusions are: (1) alcohols are much more basic than the corresponding symmetrical ethers. (2) Olefinic bonds at the α,β-position greatly increase the basicity of ketones. (3) The basicity of ethers increases as the number of α-phenyl groups decreases or as a phenyl group is shifted away from the oxygen. (4) The basicity of esters increases as the number of α-chlorine atoms decreases or as a chlorine atom is shifted away from the oxygen. (5) The basicity of para substituted acetophenones increases as the electron releasing ability of the substituent is increased in the order NO_2, Cl, H, CH_3, $(CH_3)_3C$ and CH_3O. A similar trend was established for the para substituted ethyl benzoates. (6) In $CH_3CO(CH_2)_nCOCH_3$ and $C_2H_5OCO(CH_2)_nCOOC_2H_5$ the basicity decreases rapidly as n decreases; when n is zero the basicities are far below those for the corresponding monofunctional compounds. (7) The extent to which the changes in basicity for the six groups of compounds of items (4), (5) and (6) may be quantitatively correlated with the changes in acidity of the corresponding carboxylic acids is shown graphically.

Increasing interest is being shown in the basicities of organic oxygen bases[3] as well as of the even less basic aromatic hydrocarbons.[4] Data on the basicities of these extremely weak bases have numerous important applications, *e.g.* (1) in predicting which of two functional groups will react preferentially with a proton, carbonium ion, or other acidic particle[5,6]; (2) in the separation of mixtures by con-

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[1] For the preceding article in this series see E. F. Pratt and L. Q. Green, THIS JOURNAL, **75**, 275 (1953).

[2] From the Ph.D. thesis of Ken Matsuda, Sept., 1951.

[3] Recent pertinent publications not referred to more specifically elsewhere in this paper are: E. A. Braude, *J. Chem. Soc.*, 1971 (1948); M. H. Dilke, D. D. Eley and M. G. Sheppard, *Trans. Faraday Soc.*, **46**, 261 (1950); J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Third Ed., Reinhold Publishing Corp., New York, N. Y., 1950, p. 420; S. Searles and M. Tamres, THIS JOURNAL, **73**, 3704 (1951); R. E. Van Dyke and H. E. Crawford, *ibid.*, **73**, 2018 (1951).

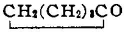
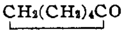
[4] The most recent references are: L. J. Andrews and R. M. Keefer, *ibid.*, **73**, 462 (1951); H. C. Brown and J. Brady, *ibid.*, **74**, 3570 (1952); V. Gold and F. L. Tye, *J. Chem. Soc.*, 2184 (1951), and other papers of this series; D. A. McCauley and A. P. Lien, THIS JOURNAL, **73**, 2013 (1951); M. Tamres, *ibid.*, **74**, 3375 (1952).

[5] F. E. Condon, *ibid.*, **74**, 2528 (1952).

[6] To be published with P. W. Erickson and with H. J. E. Segrave.

TABLE I

RELATIVE BASICITIES BY THE ETHERIFICATION METHOD

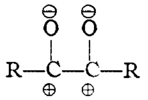
Compound	k, min.$^{-1}$ $\times 10^{-4}$
Blank	109.9
Acetophenones	
p-$C_2H_5OC_6H_4COCH_3$	41.3
p-$CH_3OC_6H_4COCH_3$	41.5
p-$(CH_3)_3CC_6H_4COCH_3$	51.1
p-$CH_3C_6H_4COCH_3$	55.1
$C_6H_5COCH_3$	61.4
2,4,6-$(CH_3)_3C_6H_2COCH_3$	63.6
p-$ClC_6H_4COCH_3$	69.9
p-$BrC_6H_4COCH_3$	72.1
m-$O_2NC_6H_4COCH_3$	93.2
p-$O_2NC_6H_4COCH_3$	97.0
Diketones	
$CH_3COCH_2CH_2COCH_3$	58.7
$CH_3COCH_2COCH_3$	72.3
$CH_3COCOCH_3$	95.4
$C_6H_5COCOC_6H_5$	105.4
Olefinic ketones	
$C_6H_5CH{=}CHCOCH{=}CHC_6H_5$	27.0
$C_6H_5CH{=}CHCOCH_3$	34.1
$(CH_3)_2C{=}CHCOCH_3$	35.5
$C_6H_5CH{=}CHCOC_6H_5$	55.8
Other ketones	
 $CH_2(CH_2)_3CO$	51.4
 $CH_2(CH_2)_4CO$	52.6
$CH_3(CH_2)_4COCH_3$	53.6
$CH_3CH_2COCH_2CH_3$	58.6
$C_6H_5COC_6H_5$	78.5
Ethyl benzoates	
p-$CH_3OC_6H_4COOC_2H_5$	68.5
p-$CH_3C_6H_4COOC_2H_5$	72.3
2,4,6-$(CH_3)_3C_6H_2COOC_2H_5$	74.6
$C_6H_5COOC_2H_5$	78.4
$C_6H_5COOCH_3$	79.6
p-$ClC_6H_4COOC_2H_5$	81.4
p-$O_2NC_6H_4COOC_2H_5$	96.8
Ethyl diesters	
$C_2H_5OCO(CH_2)_4COOC_2H_5$	40.9
$C_2H_5OCO(CH_2)_2COOC_2H_5$	52.9
$C_2H_5OCOCH_2COOC_2H_5$	64.9
$C_2H_5OCOCOOC_2H_5$	97.5
cis-$C_2H_5OCOCH{=}CHCOOC_2H_5$	67.4
trans-$C_2H_5OCOCH{=}CHCOOC_2H_5$	73.4
Ethyl chloroesters	
$CH_3(CH_2)_6COOC_2H_5$	60.0
$Cl(CH_2)_3COOC_2H_5$	76.2
$Cl(CH_2)_2COOC_2H_5$	82.0
$ClCH_2COOC_2H_5$	95.1
$Cl_2CHCOOC_2H_5$	103.9
$Cl_3CCOOC_2H_5$	112.2
Benzyl ethers	
$C_6H_5CH_2O(CH_2)_3CH_3$	65.2
$C_6H_5CH_2OCH_2C_6H_5$	81.6
$(C_6H_5)_2CHO(CH_2)_3CH_3$	91.6
$(C_6H_5)_2CHOCH(C_6H_5)_2$	98.1
$(C_6H_5)_2CHOCH_2C_6H_5$	101.6
Phenyl butyl ethers	
$C_6H_5(CH_2)_3O(CH_2)_3CH_3$	47.2
$C_6H_5(CH_2)_2O(CH_2)_3CH_3$	54.0
$C_6H_5CH_2O(CH_2)_3CH_3$	65.2
$C_6H_5O(CH_2)_3CH_3$	105.3
Dibutyl ethers	
$CH_3(CH_2)_3O(CH_2)_3CH_3$	45.6
$CH_3(CH_2)_3OCH(CH_3)CH_2CH_3$	46.0
$CH_3(CH_2)_3OC(CH_3)_3$	44.0
Substituted benzenes	
C_6H_5CN	100.3
$C_6H_5OCH_3$	100.3
$C_6H_5NO_2$	106.4
C_6H_5F	106.9
$C_6H_5OC_2H_5$	107.6
$C_6H_5CH_3$	108.0
C_6H_5Cl	110.2

version of only the most basic constituents to coordination complexes with a suitable acid[7]; (3) in interpreting recent concepts of concurrent acid–base catalysis[8]; and (4) in explaining the large changes in reaction rates which frequently result when the medium is changed.[9] In other articles of this series it was indicated that various oxygenated compounds greatly decreased the rate of reactions in benzene solution because of their ability to coördinate with and thereby deactivate the acid catalysts.[10] It occurred to us that this might be a sensitive, quantitative method for comparing the deactivating abilities or basicities of these oxygen compounds.

The self-etherification of benzhydrol was chosen as the indicator reaction because this accurately follows first-order kinetics[10,11] and because of the low basicity and ready availability of benzhydrol. One liter of benzene solution containing 0.250 mole of benzhydrol, 0.001 mole of p-toluenesulfonic acid and 0.125 mole of the oxygen base was heated under reflux. The reaction was followed by observing the rate at which the by-product water collected in a Dean–Stark trap. The oxygen bases were carefully selected in order to establish as many significant relations as possible. Table I gives the results.

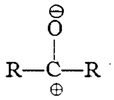
As might have been expected, the basicity of para substituted acetophenones was found to decrease as the electron releasing ability of the substituent decreased. In Fig. 1 it is shown that, except for the alkoxy compounds the basicities may be correlated quantitatively with the acidities of the corresponding benzoic acids as expressed by Hammett's σ constants.[12,13] The decreased basicity of 2,4,6-trimethylacetophenone as compared to p-methylacetophenone may best be ascribed to steric hindrance.

It was of considerable interest to find that with diketones of the series $CH_3CO(CH_2)_nCOCH_3$ the basicity decreases markedly as n decreases and that when n is zero the basicity is much less than for a typical monoketone. Similarly benzil is much less basic than benzophenone. The interaction of the carbonyl groups may be interpreted from the standpoint that the adjacent positive charges[14] cause the structure



$$\mathrm{R{-}\overset{\overset{\ominus}{O}}{\underset{\oplus}{C}}{-}\overset{\overset{\ominus}{O}}{\underset{\oplus}{C}}{-}R}$$

to be less stable than



$$\mathrm{R{-}\overset{\overset{\ominus}{O}}{\underset{\oplus}{C}}{-}R}$$

A supplementary influence may be the decreasing ability of $-(CH_2)_n-$ to release electrons to the car-

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[7] J. W. Baker and L. Hey, *J. Chem. Soc.*, 2917 (1932), and earlier papers; D. A. McCaulay, B. H. Shoemaker and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950); S. J. O'Brien and C. V. King, THIS JOURNAL, **71**, 3632 (1949), and earlier papers.

[8] C. G. Swain, *ibid.*, **70**, 1119 (1948), and later papers.

[9] S. R. Palit, *J. Org. Chem.*, **12**, 752 (1947); A. E. Remick, "Electronic Interpretations of Organic Chemistry," Second Ed., John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 272–279. The large medium effects ascribed to para substituted benzaldehydes by E. F. Pratt and E. W. Werble (THIS JOURNAL, **72**, 4638 (1950)) are supported by the large differences in basicity of the para substituted acetophenones found in the present study.

[10] See especially E. F. Pratt and J. D. Draper, *ibid.*, **71**, 2846 (1949).

[11] Actually the kinetics are *pseudo* first order since of course the rate is also affected by the catalyst concentration.

[12] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII.

[13] We wish to thank a referee for pointing out that as the basicity of the oxygen base falls to that of the benzene solvent or even lower the value of k will approach as a limit that for the blank (Table I). The absence of such a limit for the standard "ρ–σ" systems emphasizes that the correlations of Fig. 1 have no theoretical basis in the Hammett equation.

[14] This point of view was suggested by Mr. M. J. Kamlet of these laboratories.

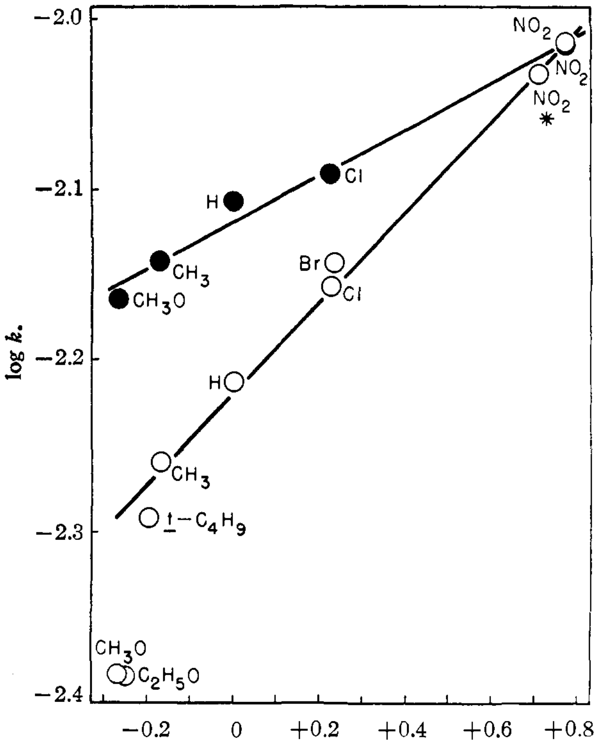

Fig. 1.—Plot of the logarithm of the rate constants for etherification in the presence of acetophenones, O and ethyl benzoates, ● (from Table I) *versus* Hammett's *sigma* constants. * This is a *meta* substituent; all others are *para*.

bonyl groups as *n* decreases; possibly steric effects are also significant.[15] In Fig. 2 it is shown that the basicities of these diketones may be correlated quantitatively with the acidities of the related diacids, $HOOC(CH_2)_nCOOH$.[16,17] It is remarkable that this correlation holds in spite of the fact that acetylacetone is almost completely enolized in benzene solution.[18]

The results for acetophenone and benzalacetone and for benzophenone, benzalacetophenone and dibenzalacetone show that insertion of a vinylene group between a phenyl and a carbonyl group increases the basicity about 25 units and insertion of a second vinylene group has an equivalent effect. It seems reasonable that these structural changes should increase the polarization of and hence the basicity of the carbonyl group.

In the foregoing cases in which ketones of closely related structures have markedly different basicities an increase in basicity often corresponds to an increase in the wave length of light absorbed by the carbonyl group in the infrared. Such an increase in the wave length absorbed has been reported as conjugated vinylene groups are introduced,[19,20] as the electron releasing ability of the para substituent of acetophenones is increased[21] and as successive methylene groups are inserted between a pair of carbonyl groups.[22,23] It should be noted, however, that there is not complete agreement on the latter point.[20]

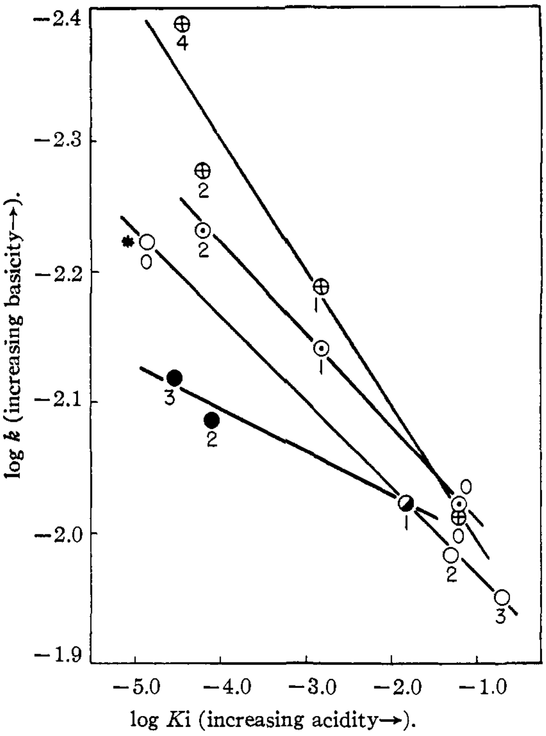

Fig. 2.—Plot of the logarithm of the rate constants for etherification in the presence of $CH_3CO(CH_2)_nCOCH_3$, ⊙, $C_2H_5OCO(CH_2)_nCOOC_2H_5$, ⊕, $Cl_xCH_yCOOC_2H_5$, O, and $Cl(CH_2)_nCOOC_2H_5$, ● (from Table I) *versus* the logarithm of the ionization constants for the corresponding dicarboxylic and chlorocarboxylic acids. The numbers under the circles give the value of *n* or *x*. * This circle is for ethyl caprylate.

The effect of varying the para substituent in ethyl benzoates is similar, although only about half as large, as that found for acetophenones. Figure 1 shows that the correlation with the acidities of the corresponding benzoic acids is quantitative. As with the acetophenones the 2,4,6-trimethyl compound is less basic than the *p*-methyl compound. The very low basicities of the "Substituted Benzenes" (Table I) show that the effects of the para substituents for both the ethyl benzoates and the acetophenones are primarily due to their differing abilities to alter the electron availability at the carbethoxyl and carbonyl groups and not to differences in electron availabilities of the substituents themselves.

With the diesters as with the diketones, and doubtless for the same reason, the basicity in-

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(15) G. F. Zellhoefer and M. J. Copley, THIS JOURNAL, **60**, 1343 (1938), report a related effect for polyethers and ascribe it to steric hindrance.

(16) The required ionization constants are available from standard sources such as the "International Critical Tables" and Landolt-Börnstein.

(17) For a general discussion of related correlations see ref. 12, pp. 222-228.

(18) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 297.

(19) R. N. Jones, P. Humphries and K. Dobriner, THIS JOURNAL, **72**, 957 (1950).

(20) R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, *ibid.*, **71**, 1068 (1949).

(21) A. H. Soloway and S. L. Friess, *ibid.*, **73**, 5000 (1951).

(22) R. N. Jones, P. Humphries and K. Dobriner, *ibid.*, **71**, 245 (1949).

(23) K. W. F. Kohlrausch and A. Pongratz, *Ber.*, **67**, 976 (1934), report a corresponding Raman shift.

creased markedly as successive methylene groups are inserted between the functional groups. Replacing the $-CH_2CH_2-$ group of diethyl succinate with either the *cis* or *trans* $-CH{=}CH-$ group greatly decreased the basicity; the conjugated olefinic bond effectively restores the ability of the carbethoxyl groups to interact.[23a] The similar basicities of diethyl maleate and diethyl fumarate are to be contrasted with the widely differing acidities of the corresponding acids. The increase in basicity on passing from diethyl oxalate to diethyl malonate corresponds to a decrease in the energy absorbed as measured by the Raman shift.[23]

Among the chloroesters there is a consistent increase in basicity as the number of α-chlorine atoms is decreased and as successive methylene groups are introduced between the chlorine atom and the carbethoxyl groups. Figure 2 shows the correlation of the basicities of the chloroesters and the saturated diesters with the acidities of the corresponding acids.[16] The basicity of ethyl caprylate might reasonably be considered to be equal to that of $Cl(CH_2)_nCOOC_2H_5$ when n is large. On this basis a curve through all the points of this series will be markedly concave toward the upper right of the plot.

Decreasing the number of α-phenyl groups or shifting a phenyl group away from the oxygen in the "Benzyl Ethers" and "Phenyl Butyl Ethers" increases their basicity much as similar variations of chlorine atoms increase the basicity of esters. The basicity varies in the related series, $C_6H_5(CH_2)_nNH_2$,[16] in a similar fashion. Substituting a secondary or tertiary butyl group for one of the primary butyl groups of di-*n*-butyl ether did not significantly affect the basicity; possibly steric and inductive effects counteract each other in this series.

The basicity of 2,6-dimethyl-γ-pyrone was so high[24] that it was necessary to use thirty-two times the standard catalyst concentration and one-half the standard oxygen base concentration in order to obtain a suitable rate of etherification. Under these conditions k was 45.3×10^{-4} min.$^{-1}$.

The self-etherification of benzhydrol could not be used as the indicator reaction for measuring the basicity of other alcohols since etherification of this other alcohol by the benzhydrol would ordinarily interfere.[10] It was possible, however, to measure approximately the relative basicity of a number of alcohols by using the dehydration of *t*-butyl alcohol as the indicator reaction. Rate constants were unobtainable for this reaction but the curves obtained upon plotting the volume of water evolved *versus* time had the same general shape so that comparison of the time required for the production of a specified yield of water gave valid relative values. Results by this method are given in Table II.

TABLE II

RELATIVE BASICITIES BY THE DEHYDRATION METHOD

Compound	"$t_{50\%}$," [a] hr.
Blank	3.6
Alcohols	
$CH_3(CH_2)_4CHOHCH_3$	16.2
$CH_3(CH_2)_8CH_2OH$	17.3
$CH_3(CH_2)_5CH_2OH$	16.2
$CH_3(CH_2)_2CH_2OH$	17.2
$C_6H_5CH_2OH$	5.9
Ethers	
 $CH_2CH_2OCH_2CH_2O$	10.1
$CH_3(CH_2)_3O(CH_2)_3CH_3$	7.2
$CH_3(CH_2)_3OCH_2C_6H_5$	3.8
$C_6H_5CH_2OCH_2C_6H_5$	3.8
$CH_3(CH_2)_3OCH(C_6H_5)_2$	3.8
$C_6H_5CH_2OCH(C_6H_5)_2$	3.3
Other compounds	
$(C_6H_5)_2NH$	65.4
$CH_3(CH_2)_6COOC_2H_5$	6.4
C_6H_5CN	5.3
C_6H_5Cl	4.3

[a] See Experimental for exact definition of this symbol.

In contrast to predictions based on the inductive effect alcohols were found to be much more basic than their symmetrical ethers. This may well be due to the decreased steric hindrance of the hydrogen atom as compared to the alkyl groups.[25] Little difference in basicity was found among normal primary alcohols of varying molecule weights or between primary and secondary alcohols. Benzyl *n*-butyl ether was again found to be much less basic than di-*n*-butyl ether but introduction of additional phenyl groups had little effect.

Attempts were made to correlate our relative basicity data with the limited amount of data in the literature on the basicity of the same compounds. For acetophenone and the para bromo and para methyl compounds the correlation with the results obtained *via* ultraviolet absorption methods was quite satisfactory.[26] Except for diethyl oxalate there was rough general agreement with data for seven of the compounds based on their solubility in dichlorofluoromethane.[27] The correlation for eighteen compounds studied by an infrared absorption method involving bond formation with deuterated methanol was very approximate at best, but for seven compounds studied by a similar method using hydrogen chloride for the bond formation[28] the correlation was somewhat better.

The distillation method of determining relative basicities using the self-etherification of benzhydrol as the indicator reaction is facile and sensitive. The sensitivity is no doubt primarily due to the fact that the benzene solvent, in contrast to most oxygenated solvents, coördinates with the acid catalyst much less effectively than does the added

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(23a) NOTE ADDED IN PROOF.—The similarities between these diesters and diketones as well as between the *para* substituted ethyl benzoates and acetophenones are most simply interpreted on the basis that the carbonyl oxygen contributes more to the basicity of the esters than does the ethoxyl oxygen. This is in agreement with the recent results of S. Searles, M. Tamres and G. M. Barrow, THIS JOURNAL, **75**, 71 (1953).

(24) This appears to be the strongest oxygen base known. H. N. K. Rordam, THIS JOURNAL, **37**, 557 (1915), found its ionization constant to be 1.9×10^{-14}.

(25) Our results are consistent with those of J. Hine and M. Hine, *ibid.*, **74**, 5266 (1952), who discuss this question in detail.

(26) Ref. 12, p. 271. See also p. 266.

(27) G. F. Zellhoefer, M. J. Copley and C. S. Marvel, THIS JOURNAL, **60**, 1337, 2666 (1938).

(28) W. Gordy, *J. Chem. Phys.*, **9**, 215 (1941), and earlier papers.

oxygen base. The results are expressed by a single easily interpreted number and the bases are compared under the same conditions, *i.e.*, in dilute solution in benzene.[29] Other papers in this series have shown that many reactions are advantageously carried out under conditions similar to those used here so that the data are directly usable and have already been applied to controlling the course of reactions.[6] The distillation method can be used for both solids and liquids and should be applicable to the study of a variety of other extremely weak bases; with suitable modification it may be useful for determining the relative acidity of extremely weak acids as well.

Experimental[30]

Preparation and Purification of Materials.—All constituents of the reaction mixtures were carefully purified by standard methods until the refractive indices or melting points agreed closely with the literature data with the following exceptions.

The β-phenylethyl *n*-butyl ether appears to be a new compound. It was prepared by dropwise addition of *n*-butyl bromide (157 g.) to the refluxing mixture resulting from the treatment of 122 g. of β-phenylethyl alcohol with 23.0 g. of sodium in 1 l. of toluene. After it had been heated under reflux with stirring for three days the mixture was cooled, the precipitate filtered off and most of the solvent removed by distillation. The residue was treated with a small amount of sodium to remove unreacted alcohol and the resulting alkoxide was filtered off. The filtrate was distilled from sodium through a 9-in. Vigreux column; b.p. 112.0–113.0° (13 mm.), $n^{25}\text{D}$ 1.4829.

Anal.[31] Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 81.00; H, 10.18.

γ-Phenylpropyl *n*-butyl ether also appears to be new and it was prepared by a similar procedure. The product was distilled through a 7-in. Vigreux column; b.p. 128.5–130.0° (15 mm.), $n^{25}\text{D}$ 1.4817.

Anal. Calcd. for $C_{13}H_{20}O$: C, 81.19; H, 10.48. Found: C, 81.06; H, 10.56.

Purified *p*-chloroacetophenone had $n^{25}\text{D}$ 1.5523 but no literature value was found. The boiling point was 231.8–232.7° as compared to a literature value of 232°.

Effect of Varying the Concentrations of Catalyst and of Oxygen Base.—It had been previously found[6] that doubling the catalyst concentration approximately tripled the rate of etherification of benzhydrol by *n*-butyl alcohol under the conditions of this distillation method. Similar results were obtained in this investigation for the self-etherification of benzhydrol. Thus under the standard conditions (below) but with no oxygen base present the rate constant increased from 11.36 to 34.5 to 109.9 min.$^{-1}$ × 10^{-4} as the catalyst concentration was increased from 0.00025 to 0.0005 to 0.001 mole per l. With the standard concentration of ethyl benzoate present (0.125 mole per l.) the rate constant increased from 27.6 to 78.4 min.$^{-1}$ × 10^{-4} as the catalyst concentration was increased from 0.0005 to 0.001 mole per l.

When the catalyst concentration was held constant at 0.001 mole per l. and the concentration of oxygen base was doubled the rate constant decreased by about 25%. An increase in the concentration of acetophenone from 0.0625 to 0.125 to 0.250 mole per l. lowered the rate constant from 80.0 to 61.4 to 46.4 min.$^{-1}$ × 10^{-4}. It is pertinent to note in this regard that it can be calculated on the basis of the equilibrium $\text{B:} + \text{HA} \rightleftarrows \text{B:HA}$ in which B: is the oxygen base and HA is the acid catalyst that doubling the total amount of base reduces the concentration of free acid by less than one-half.

Consideration of Possible Side Reactions.—The oxygen bases selected for this study were those which would not be expected to undergo side reactions under the conditions used.[32] It was also important that the bases should not be both volatile and water soluble so that they would not appear in the aqueous phase.

In order to demonstrate the absence of serious side reactions approximately half of the oxygen bases of Table I were recovered in over 90% yield after the determination was complete. It was unnecessary to recover many of the compounds since prior recovery of closely related or even more reactive compounds of the class showed the absence of side reactions. In certain cases the oxygen bases were solids difficult to separate from the dibenzhydryl ether formed or low boiling liquids difficult to separate quantitatively from the benzene, but in no case was there reason to feel that these were more reactive than related compounds which were recovered satisfactorily. Among the oxygen bases recovered in over 90% yield were diethyl oxalate, diethyl fumarate, ethyl trichloroacetate, ethyl anisate, *p*-ethoxyacetophenone, *p*-nitroacetophenone, acetonylacetone, benzalacetone, phenyl *n*-butyl ether and benzhydryl *n*-butyl ether. The dibenzhydryl ether was also recovered in about 95% yield in numerous cases.

The almost exactly quantitative yield of water obtained in most cases (see below) also indicated that side reactions did not occur to a significant extent. The satisfactory rate constants supported this conclusion as did the consistent trends within a series of compounds and the quantitative correlations with relative acidities (Figs. 1 and 2). Since the same or related trends were observed for ketones, esters and ethers, while any side reactions could hardly be the same, the absence of side reactions is again indicated.

The foregoing discussion applies directly to the experiments carried out by the etherification method, but similar considerations plus the high yield of isobutene obtained showed the absence of side reactions in experiments by the dehydration method.

Standard Procedure Using Etherification as the Indicator Reaction.—One-fourth mole of benzhydrol and 0.125 mole of the oxygen base were dissolved in benzene in a 1-l. volumetric flask. The solution was kept in a water-bath at 25° for 20 minutes and the flask filled to the mark with more benzene which had been held at 25°. The solution was transferred to the 2-l. reaction vessel and the flask rinsed with benzene equivalent in volume to the volume of liquid retained in the Dean–Stark water separator. About 1 ml. of water was added to the separator and the apparatus assembled as previously described.[10] After refluxing to remove any traces of water a 1-ml. beaker containing 0.001 mole of *p*-toluenesulfonic acid monohydrate was dropped in. Heat was applied to the hemispherical mantle, the voltage being maintained at 70 in all cases, and the flask was swirled 1 min. to ensure complete mixing. Frequent readings of the water volume *versus* time were taken over the 20 to 80% portion of the reaction.

The water separators were recalibrated and all the precautions previously described[10] were taken. A looped chromel wire was used to eliminate any irregularities in the meniscus and to displace any water droplets from the inner surface of the condenser. Refluxing was allowed to continue overnight in order to determine the total amount of water which would be evolved. In over 90% of the cases the yield of water was 100 ± 1% of the theoretical value. Only in the experiments with acetylacetone (water yield, 106%) did the yield of water differ by more than 2.5% from the theoretical value.

Recalibrated thermometers were used and the temperature variation was not more than ±0.2° for the 20 to 80% portion of a given determination; for over 95% of the experiments the variations were within ±0.1°. Among all of the experiments the temperature was 81.4 ± 0.5° while among most of them it was 81.4 ± 0.3°. The value given for the rate constant for the blank (Table I) is the average of quadruplicate determinations; the extreme values among these were 109.0 and 110.6 min.$^{-1}$ × 10^{-4}. Duplicate determinations for several of the oxygen bases showed that the rate constants could readily be checked to within ±2%.

The rate constants were calculated for the 20 to 80% portion of the reaction by the graphical method based on the equation $k = (2.303/t) \log a/(a - x)$ in which a is the original concentration of benzhydrol and $a - x$ is the con-

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[29] The importance of this is emphasized by G. W. Wheland, "Advanced Organic Chemistry," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 78.

[30] All melting points are corrected.

[31] We wish to thank Prof. Mary Aldridge and Mr. Byron Baer for all the microanalyses reported herein.

[32] Unpublished work with Dr. L. Q. Green showed that ketal formation is negligible under these conditions.

centration at time t, in minutes. In about 90% of the cases a plot of log $a/(a - x)$ *versus* t gave a straight line for the 20 to 80% portion of the reaction while the linear portion was about 10% less than this for the remainder of the cases. Multiplication of the slope of the line by 2.303 gave k.

Standard Procedure Using Dehydration as the Indicator Reaction.—The procedure was very similar to that just described except that the reaction mixture consisted of 500 ml. of a benzene solution containing 0.125 mole of *t*-butyl alcohol, 0.125 mole of the oxygen base and 0.008 mole of *p*-toluenesulfonic acid monohydrate. The isobutene which was evolved as the reaction proceeded was, in a number of cases, absorbed in concentrated sulfuric acid and weighed. A 93 to 96% yield was obtained in each case tested.

It was found that more reproducible results could be obtained if "zero" time was taken when 0.29 ml. of water had collected. This is 0.15 ml. (6.67%) more than the water of crystallization of the catalyst. A plot of the per cent. yield of water *versus* time gave a smooth curve the slope of which increased with time until the reaction was over 97% complete; obviously no rate constant could be calculated. A plot of the per cent. yield of isobutene *versus* time gave a curve of the same shape but this curve lagged as much as 10% behind the curve based on water evolution. The times required for the reaction to proceed from 6.67 to 50.0% completion were chosen to compare the rates. This is denoted "$t_{50\%}$" in Table II for the sake of brevity.

There was a gradual increase in temperature as the reaction progressed and the temperature variations were larger than for the etherification method. For over 85% of the experiments the variation within an experiment was not more than ±0.3° for the 6.67 to 50% portion of the reaction. Among all the experiments the temperature was 80.9 ± 1.5° and among most of them it was 80.9 ± 0.8°. The yield of water was usually within 1% and always within 3% of the theoretical value except for the control which for some unexplained reason gave a 96% yield consistently. The values given in Table II for the control and for the alcohols and ethers are the average of duplicate determinations which agreed to within 5 to 8%.

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COLLEGE PARK, MD.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO]

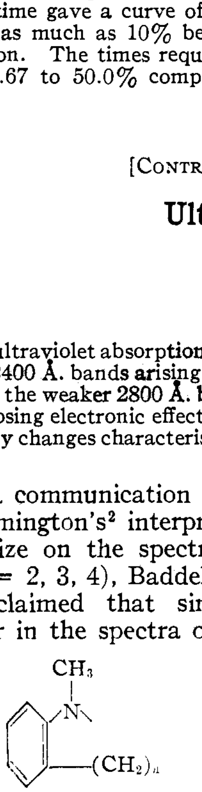
Ultraviolet Absorption Spectra of Hindered Ketones[1]

BY GREGORY D. HEDDEN AND WELDON G. BROWN

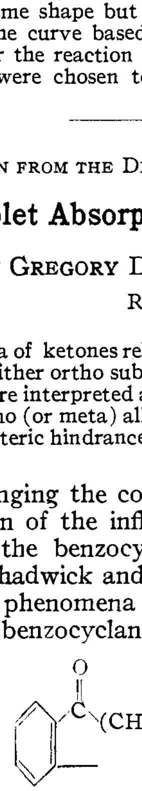
RECEIVED MARCH 21, 1953

The ultraviolet absorption spectra of ketones related to acetophenone show well-defined steric effects (decreased intensity) in the 2400 Å. bands arising from either ortho substitutions or excessive branching (tertiary ketones). The intensity variations in the weaker 2800 Å. bands are interpreted as the resultant of a normal steric effect related to carbonyl aplanarity and an opposing electronic effect of ortho (or meta) alkyl groups. In the series of cyclic ketones beginning with α-indanone the intensity changes characteristic of steric hindrance appear in benzosuberone and, to a greater degree, in benzocycloöctanone.

In a communication challenging the correctness of Remington's[2] interpretation of the influence of ring size on the spectra of the benzocyclamines (I, n = 2, 3, 4), Baddeley, Chadwick and Rawlinson[3] claimed that similar phenomena do not appear in the spectra of the benzocyclanones (II, n = 2, 3, 4). They quoted previously published[4] data and their own (unpublished) data as supporting this conclusion, but did not present a detailed analysis. Nor did they explain why their interpretation of the amine spectra, based upon the steric requirements for hyperconjugation, should not apply equally to the analogous cyclic ketones.



I



II

In this paper it will be shown that the spectroscopic variations in the ketone series closely parallel those in the amines if analogous transitions are compared, and the gross effects are related to the degree of aplanarity of the carbonyl group. The pattern of steric effects will first be established with respect to ketones of the acetophenone series in which hindrance is produced by methyl groups on the ortho positions. The experimental data are new for although Biquard[4] recorded the spectra of the bicyclic ketones (II, n = 2, 3, 4) in alcohol and in cyclohexane solution, we have extended the series and have taken *n*-heptane as the solvent throughout.

For convenience the absorption bands in the accessible ultraviolet will be designated, in order of decreasing wave length (and increasing intensity), as K (for ketone, excitation of non-bonding oxygen electrons), B (for benzene ring absorption) and C (for conjugation, N → V transition). Attention is focussed upon the strong C bands, occurring at about 2400 Å., which like the strong 2500 Å. bands of the aromatic amines, most clearly reflect the geometrical relationship between the benzene ring and the carbonyl (or dialkylamino) group. The dependence of the B bands upon steric factors will be discussed later. The faint K bands, which have no counterpart in the amine spectra, have not been studied in detail.

The oscillator strength, f, for the C transition of a nuclear-methylated derivative of acetophenone may be represented by $f = f^\circ + f_{\text{para}} - f_{\text{ortho}}$, where f° is the observed oscillator strength for acetophenone (0.22, *cf.* Table I, also Fig. 1 and 2), f_{para} is the normal intensifying effect of para methyl group and f_{ortho} is the opposing effect of a methyl group in the ortho position. With the assump-

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[1] Abstracted from the Ph.D. Dissertation of Gregory D. Hedden, The University of Chicago, June, 1951.

[2] W. R. Remington, THIS JOURNAL, **67**, 1838 (1945).

[3] G. Baddeley, J. Chadwick and S. B. Rawlinson, *Nature*, **164**, 833 (1949).

[4] D. Biquard, *Bull. soc. chim. France*, [5] **8**, 55 (1941).