Reaction Rates by Distillation. XI. The Accelerating Effect of Certain Nitro and Cyano Compounds on the Self-Etherification of Benzhydrol in Benzene

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It was unexpectedly found that *o*-dinitrobenzene, under the conditions[4,5] given for Table I, caused a 50% increase in the rate of self-etherification of benzhydrol. *o*-Dicyanobenzene gave a 29%, malononitrile an 80%, and tetracyanoethylene[6] a 105% increase in rate. The effects for a total of 38 selected nitro and cyano compounds as well as 11 other compounds were determined (Table I).

Steric factors appear to be of primary importance, since among the dinitrobenzenes and certain related compounds the effect decreased markedly as the substituents were shifted from the *ortho* to the *meta* to the *para* positions. No monofunctional compound had a large accelerating effect.

When the electron-attracting ability of two identical *ortho* substituents was decreased in the order NO_2, CN, Cl, H, and CH_3O, the rate of etherification decreased consistently from 50% acceleration to 28% deceleration; phenylacetonitriles with various substituents in the *para* position gave a similar consistent decrease in the etherification rate. It is to be noted that the *p*-toluenesulfonic acid catalyst was added only after the other components of the reaction mixture had been heated under reflux for 1 hr. and etherification never occurred during this period.

The results listed in Table II show that *o*-dinitrobenzene also gave large accelerating effects when the ether being formed was changed to dianisyl, difluorenyl, or triphenylmethyl butyl ether as well as when the catalyst was changed to methanesulfonic acid. The accelerating effect of *o*-dinitrobenzene was proportional to its amount (Table II). It was also found that the accelerating effect of *s*-trinitrobenzene increased markedly when the solvent was changed from benzene to cyclohexane.

The large decreases in rate shown by several of the compounds listed in Table I can be explained fairly satisfactorily as deactivation of the catalyst *via* its coordination with unshared electron pairs as previously proposed.[5] Since our knowledge concerning the many solvation equilibria which may be involved is very limited, it is, perhaps, not surprising that attempts to explain the accelerating effects on the basis

TABLE I. EFFECT OF SELECTED COMPOUNDS ON THE RATE OF SELF-ETHERIFICATION OF BENZHYDROL[a,b]

Compound	k, min.$^{-1}$ × 10^{-4}
Mono- and Dinitrobenzenes	
$C_6H_5NO_2$	111
p-$CH_3C_6H_4NO_2$	109
o-$C_6H_4(NO_2)_2$	151
m-$C_6H_4(NO_2)_2$	124
p-$C_6H_4(NO_2)_2$	111
o-$NCC_6H_4NO_2$	116
m-$NCC_6H_4NO_2$	112
p-$NCC_6H_4NO_2$	103
o-$ClC_6H_4NO_2$	120
m-$ClC_6H_4NO_2$	117
p-$ClC_6H_4NO_2$	101
o-$CH_3OC_6H_4NO_2$	118
p-$CH_3OC_6H_4NO_2$	109
m-$CH_3OC_6H_4NO_2$	102
Trinitrobenzenes	
1,3,5-$(O_2N)_3C_6H_3$	132
2,4,6-$(O_2N)_3C_6H_2Cl$	129
2,4,6-$(O_2N)_3C_6H_2OCH_3$	118
2,4,6-$(O_2N)_3C_6H_2CH_3$	111
Mono- and Dicyanobenzenes	
C_6H_5CN	97
p-$CH_3OC_6H_4CN$	87
p-$CH_3C_6H_4CN$	85
o-$C_6H_4(CN)_2$	130
m-$C_6H_4(CN)_2$	102
p-$C_6H_4(CN)_2$	94
Phenylacetonitriles	
p-$O_2NC_6H_4CH_2CN$	134
p-$ClC_6H_4CH_2CN$	98
$C_6H_5CH_2CN$	91
p-$CH_3OC_6H_4CH_2CN$	62
$(C_6H_5)_2CHCN$	96
Other Cyano Compounds	
$NCCH_2CN$	182
$NCCH_2CH_2CN$	130
CH_3CH_2CN	78
$(NC)_2C{=}C(CN)_2$	208
$C_6H_5CH{=}C(CN)_2$	115
Aliphatic Nitro Compounds	
CH_3NO_2	106
$CH_3CH_2CH_2NO_2$	106
$CH_3CH(NO_2)CH_3$	103
$\underline{CH_2CH_2CH_2CH_2CH_2CH}NO_2$	92
Dimethoxybenzenes	
m-$C_6H_4(OCH_3)_2$	102
p-$C_6H_4(OCH_3)_2$	87
o-$C_6H_4(OCH_3)_2$	72
Chlorine and Sulfur Compounds	
o-$C_6H_4Cl_2$	106
$O{=}C_6Cl_4{=}O$[c]	105
$Cl_2C{=}CCl_2$	100
$C_6H_5SO_2C_6H_5$	85
$C_6H_5SO_2CH_2C_6H_5$	76
Hydrocarbons	
1,3,5-$C_6H_3(CH_3)_3$	104
$\underline{C_6H_4CH{=}C_6H_4{=}CH}$[d]	104
1,2,4,5-$C_6H_2(CH_3)_4$	102

[a] One liter of a benzene solution containing 0.250 mole of benzhydrol, 0.001 mole of *p*-toluenesulfonic acid, and 0.125 mole of the compound being tested was heated under reflux while the by-product water was distilled into a trap. [b] Control, $k = 101$ min.$^{-1}$ × 10^{-4}. [c] Chloranil. [d] Anthracene.

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[1] From the Ph.D. Thesis of D. G. Jones, University of Maryland, May 1961.

[2] We wish to thank the National Science Foundation for a Cooperative Fellowship (to D. G. J.) which greatly aided the progress of this work.

[3] For the preceding paper in this series, see E. F. Pratt and M. J. Kamlet, *J. Org. Chem.*, **28**, 1366 (1963).

[4] The same conditions were used previously[5] for determining the decelerating effect of ketones, esters, ethers, and alcohols.

[5] E. F. Pratt and K. Matsuda, *J. Am. Chem. Soc.*, **75**, 3739 (1953).

[6] We wish to thank Dr. B. C. McKusick of Du Pont for a sample of this compound.

TABLE II. EFFECT OF *o*-DINITROBENZENE ON THE RATE OF SEVERAL ETHERIFICATION REACTIONS

o-$C_6H_4(NO_2)_2$, moles	p-$CH_3C_6H_4SO_3H$, moles	k, min.$^{-1}$ × 10^{-4}
Benzhydrol Self-Etherification		
0.000	0.001	101
0.0625	0.001	123
0.125	0.001	151
0.250	0.001	196
0.000	0.0015[a]	155
0.125	0.0015[a]	198
Anisyl Alcohol Self-Etherification		
0.000	0.002	192
0.125	0.002	256
Fluorenol Self-Etherification[b]		
0.000	0.016	130
0.125	0.016	161
Etherification of *n*-Butyl Alcohol by Triphenylcarbinol		
0.000	0.001	146
0.125	0.001	250

[a] Methanesulfonic acid replaced the *p*-toluenesulfonic acid. [b] Total yield of water was 110–115% indicating that some alkylation of the benzene solvent occurred.

of the dipole moment of the added compounds,[7-9] on their effectiveness as electron acceptors in the formation of charge transfer complexes,[10-12] or on their ability to act as polyfunctional catalysts[13] met with only very limited success.

Experimental Section

Starting Materials.—All constituents of the reaction mixtures were carefully purified by standard methods until their refractive indices or melting points agreed closely with the literature data except for diphenyl sulfone. Repeated recrystallization of it gave a product which melted at 124.5–125.5°, although the literature lists values as high as 128–129°.

Experiments of Table I.—The standard procedure employed for all the experiments of Table I was in all significant respects identical with that previously described[5] except the benzene solution of the benzhydrol and the compound being studied was adjusted to 990 ml. instead of 1000 ml. A volumetric flask recalibrated at 990 ml. was used for this and, after refluxing the solution 1 hr., 10 ml. of a 0.1 *M* solution of *p*-toluenesulfonic acid in benzene was added This standard solution of acid was prepared by refluxing 0.1 mole of *p*-toluenesulfonic acid monohydrate in 995 ml. of benzene, in a flask fitted with a water separator, for 3 hr. during which the water of hydration was evolved and the acid was dissolved. Extreme care was taken during the storage and addition of this solution (from a 25-ml. buret) to keep it anhydrous. Adding the catalyst in this way circumvented difficulties encountered in accurately weighing small amounts of the very hygroscopic solid catalyst.

In the previously described procedure[5] it was necessary to insert a looped Chromel wire through the top of the condenser to displace any water droplets from its interior before each reading of the volume of water. This was found to be unnecessary if the condenser and water trap were scrubbed thoroughly first with detergent, then with scouring powder, and finally with both and then rinsed carefully.[14] This was done within 2 hr. of the time they were to be used and during this period the apertures were closed with aluminum foil so that the inner surfaces remained wet.

All precautions of the earlier study[5] were taken. The benzhydrol used was recrystallized in a single batch. Five separate determinations of the rate constant for the control over a period of several months gave a value of 101.2 ± 1.1 min.$^{-1}$ × 10^{-4}. Numerous repeat experiments showed the values in Table I were reproducible to within 2.3%. The temperature variation over the 20–80% portion of a given experiment was within ±0.1° in all but three cases. Among all the experiments the temperature was usually 82.1 ± 0.3° and almost invariably 82.1 ± 0.5°. The total yield of water was usually 100 ± 1%; in all except three cases for which it was 103% and one case (*m*-dimethoxybenzene) for which it was 110%, the yield of water was 100 ± 2%.

It was noted that the addition of benzhydrol to a solution of tetracyanoethylene in benzene deepens the color from lemon yellow to orange. The total yield of water in the tetracyanoethylene experiment (Table I) was 102% and at the end of the experiment the tetracyanoethylene was recovered in over 80% yield.

In most cases the plot of log $a/(a - x)$ *vs.* t gave a straight line for approximately the 20–80% portion of the reaction. The slope of this line was multiplied by 2.303 to give the value of k.

Supplementary Experiments.—The modifications of the above standard procedure required for the experiments of Table II are readily apparent with the following exceptions.

In the experiments with fluorenol the catalyst was added as the solid. In spite of the excessive yields of water a straight line was obtained for the 10–70% portion of the reaction.

In the etherification of *n*-butyl alcohol by triphenylcarbinol 0.125 mole of each of the alcohols was used.

The catalyst (0.001 mole) was also added as a solid in the experiments using cyclohexane in place of benzene as the solvent. In these experiments the kinetics shifted toward zero order and the reproducibility of the rates was poor. For the fastest of three controls the time required for the evolution of a 50% yield of water was 101 min., while with 0.05 mole of *s*-trinitrobenzene present the time was only 49 min. Only 0.05 mole instead of the standard 0.125 mole of *s*-trinitrobenzene was added to 1 l. of reaction mixture because of the limited solubility of the nitro compound in cyclohexane. The cyclohexane was purified by washing it with concentrated sulfuric acid and then with water and distilling it as for benzene. The temperature for the experiments in cyclohexane was 82.2 ± 0.2° and the total yield of water was 100%.

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(7) "Dipole Moments," Appendix, compiled by N. U. Sidgwick, published for the Faraday Society, Gurney and Jackson, London, 1940.

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Temperature Dependence of the Conformational Equilibria of Cyclic Sulfites

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Hellier, *et al.*,[1] suggested that the S=O group in six-membered cyclic sulfites is more stable in the axial rather than the equatorial conformation. They have identified the 1190-cm.$^{-1}$ band with an axial S=O and the 1230-cm.$^{-1}$ band with an equatorial S=O. Two geometric isomers of *meso*-2,4-pentanediol cyclic sulfite were isolated by Pritchard, *et al.*[2,3] The more stable one, isomer I, had the S=O band at *ca.* 1190 cm.$^{-1}$, and the less stable one, isomer II, had the main S=O absorption at 1230 cm.$^{-1}$. Thermal equilibration of the isomers yields mainly I. Pritchard, *et al.*,[3]

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