The Influence of the Solvent on Organic Reactivity. Part 5.[1] Kinetics of the Reaction of Diazodiphenylmethane with Benzoic Acid in Branched-chain Alkanols and in Electronegatively Substituted Alcohols

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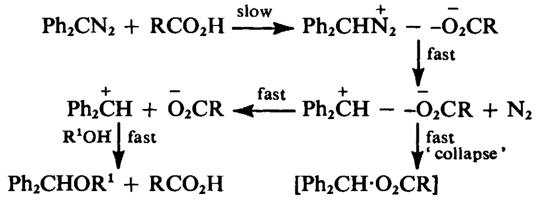
Rate coefficents at 30.0 °C are presented for the reaction of diazodiphenylmethane and benzoic acid in five branched-chain alkanols and in nine electronegatively substituted alcohols. As in earlier work, correlation analysis of log *k* values involves multiple regression on the σ^* value of the group R^1 in the alcohol R^1OH, the Kirkwood function of dielectric constant $f(\varepsilon) = (\varepsilon - 1)/(2\varepsilon + 1)$, and $n_{\gamma H}$, the number of hydrogen atoms in the γ-position of the alcohol. The results for branched-chain alcohols provide further examples of the acceleratory effect of γ-hydrogen atoms. A correlation equation based on 27 alkanols and phenyl-substituted alcohols, for which σ^* lies between −0.325 and +0.215, can be applied with reasonable success to seven electronegatively substituted alcohols, for which σ^* lies in the range 0.07—0.92. 2-Methoxy- and 2-phenoxy-ethanol show marked deviations. Correlation equations properly incorporating the data for the electronegatively substituted alcohols are finally presented.

Earlier papers[2] and those of other authors[3] showed that the rate-determining step in the reaction between diazodiphenylmethane (DDM) and carboxylic acids in alcohols involves a proton transfer from carboxylic acid to DDM to form a diphenylmethanediazonium–carboxylate ion-pair. Subsequent fast, product-governing stages probably involve the intervention of a diphenylmethyl–carboxylate ion-pair;[3–5] this may then either 'collapse' to give the ester or react with the solvent to give an ether (see Scheme).

In Part 14 of another series[6] we presented the second-order rate coefficients at 30.0 °C for the reaction of DDM with benzoic acid in 22 alcohols (variously primary, secondary, or tertiary aliphatic alcohols, or phenyl-substituted alcohols). As in earlier work[7] the log *k* values were subjected to correlation analysis through multiple regression on $f(\varepsilon)$ [the Kirkwood function $(\varepsilon - 1)/(2\varepsilon + 1)$ of dielectric constant[8]], σ^* (the Taft polar constant for the alkyl group of the alcohol[9]), and $n_{\gamma H}$ (the number of γ-hydrogen atoms in the alcohol). The regression equation was (1)[6] with multiple correlation

$$\log k = -1.484 + \underset{(\pm 0.474)}{3.957 f(\varepsilon)} + \underset{(\pm 0.099)}{3.055\sigma^*} + \underset{(\pm 0.007)}{0.029 n_{\gamma H}} \qquad (1)$$

coefficient, *R* 0.993, and standard deviation of the estimate, *s* 0.053. The terms of the equation are interpreted as follows.[7] A favourable influence of dielectric constant is expected for a reaction in which passage from initial to transition state involves charge separation, but stepwise regression shows that the σ^* term is the more important. This indicates the dominant role of the solvating properties of the alcohol, *i.e.* Lewis basicity or acidity of the solvent.† The term $n_{\gamma H}$, which is of minor importance overall, signifies a steric moderation of the basic properties of the alcohol oxygen. For certain alcohols it has a strong effect, *e.g.* the reaction is considerably faster in 2-methylbutan-1-ol than in ethanol, even though the former has the lower dielectric-constant and the more negative value of σ^*: for 2-methylbutan-1-ol, $n_{\gamma H} = 6$, whereas for ethanol $n_{\gamma H} = 0$.



Scheme.

In the present work, the acceleratory effect of γ-hydrogen atoms was further studied through measurements involving branched-chain alcohols. The study was also extended to nine alcohols XCH_2OH, in which X is an electron-attracting substituent such that the σ^* value of XCH_2 lies in the range 0.07—0.92. In the earlier work[6,7] the σ^* value was restricted to the range −0.31 to +0.215, and only the phenyl-substituted alcohols had $\sigma^* > 0.00$.

Discussion

The Solvent Effect of Branched-chain Alcohols on the Reaction of Diazodiphenylmethane with Benzoic Acid.—Rate coefficients at 30.0 °C and solvent parameters for correlation analysis are given in Table 1. (Corresponding values for alcohols 1—22 are given in Table 1 of ref. 6.) We draw special attention to the data for 2,2-dimethylpropan-1-ol (neopentyl alcohol). This solvent is a solid at 30 °C. The rate coefficient was measured for reaction in ethanol–neopentyl alcohol mixtures, of mole fraction x_{EtOH} between 0.16 and 0.42. The notional value for liquid neopentyl alcohol was then obtained by extrapolation to $x_{EtOH} = 0$ on a low-gradient, rectilinear plot of log *k versus* x_{EtOH}. The solvents 23—27 include three β-branched primary alcohols (nos. 23—25), a secondary alcohol (no. 26), and a tertiary alcohol (no. 27).

Multiple regression of log *k* on $f(\varepsilon)$, σ^*, and $n_{\gamma H}$ for solvents 1—27 gives equation (2). Comparison with equation (1) shows

$$\log k = -1.408 + \underset{(\pm 0.350)}{3.760 f(\varepsilon)} + \underset{(\pm 0.104)}{3.122\sigma^*} + \underset{(\pm 0.0045)}{0.046 n_{\gamma H}} \qquad (2)$$
$$R = 0.992 \qquad s = 0.057$$

that the five extra data points have been accommodated with only a trivial decrease in *R* and increase in *s*. The coefficients of the $f(\varepsilon)$ and σ^* terms have also been changed only slightly,

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† The positive sign of the regression coefficient of σ^* in equation (1) is explained as follows. The $^-CO_2H$ proton is solvated by the oxygen of R^1OH, while the nascent $^-CO_2^-$ is solvated by the hydrogen of R^1OH. The former effect hinders the transfer of the proton to the DDM and is enhanced by electron-releasing groups as R^1, while the latter effect assists the proton transfer and is enhanced by electron-attracting groups as R^1. Hence, as the value of σ^* for R^1 is made less negative or more positive, log *k* is increased.

Table 1. Rate coefficients (l mol^{-1} min^{-1}) for the reaction between diazodiphenylmethane and benzoic acid in highly branched alcohols at 30.0 °C

No.	Solvent	k	ε [c]	σ^* [d]	$n_{\gamma\text{H}}$ [e]
23	2-Methylbutan-1-ol	1.35	14.7	−0.14	5
24	2,2-Dimethylpropan-1-ol	1.96 [a]	14	−0.14	9
25	2,2-Dimethylbutan-1-ol	1.29 [b]	9.0	−0.15	8
26	3,3-Dimethylbutan-2-ol	0.41	4.55	−0.24	9
27	2,3-Dimethylbutan-2-ol	0.112	3.63	−0.325	6

[a] By extrapolation from values for mixtures with ethanol (see text and Experimental section). [b] Ref. 7. Result not previously used in multiple regression. [c] Dielectric constant: no. 23, 25 °C; no. 24, estimated from values for related compounds, 25 °C; no. 25, 23 °C, measured by Mr. C. E. Reed, Department of Physics, University of Hull; nos. 26 and 27, 19 °C, measured in present work (see Experimental section). [d] Polar substituent constant of alkyl group, mainly estimated from those of related groups. [e] Number of γ-hydrogen atoms.

Table 2. Comparison of log k(obs.) and log k(calc.) [from equation (2)] for reaction between diazodiphenylmethane and benzoic acid in alcohols for which $n_{\gamma\text{H}} \geqslant 5$

No.	Solvent	$n_{\gamma\text{H}}$	log k(obs.)	log k(calc.)
7	2-Methylpropan-1-ol	6	0.211 [a]	0.201
10	Pentan-3-ol	6	−0.262 [a]	−0.175
23	2-Methylbutan-1-ol	5	0.130	0.079
24	2,2-Dimethylpropan-1-ol	9	0.292	0.250
25	2,2-Dimethylbutan-1-ol	8	0.111	0.072
26	3,3-Dimethylbutan-2-ol	9	−0.387	−0.427
27	2,3-Dimethylbutan-2-ol	6	−0.951	−0.953

[a] Ref. 6.

but the coefficient of $n_{\gamma\text{H}}$ is increased from 0.029 to 0.046. In stepwise regression σ^* enters first ($r = 0.927$), followed by f(ε) ($R = 0.952$). The partial correlation coefficients for the introduction of f(ε) after σ^* and for the introduction of $n_{\gamma\text{H}}$ after σ^* and f(ε) are 0.58 and 0.90, respectively, both being significant at above the 99.9% level.

Detailed comparison of log k(obs.) and log k(calc.) shows that equation (2), with its enhanced coefficient of $n_{\gamma\text{H}}$, is very effective in expressing the acceleratory influence of γ-hydrogen atoms; see Table 2.

The Solvent Effect of Electronegatively Substituted Alcohols on the Reaction of Diazodiphenylmethane with Benzoic Acid.—Rate coefficients at 30.0 °C and solvent parameters for correlation analysis are given in Table 3. We draw special attention to the data for 2,2,2-trifluoroethanol (TFE). This solvent is itself sufficiently acidic to react very rapidly with DDM and it is quite impossible to study the reaction of DDM with benzoic acid in TFE alone. The use of mixtures of TFE and ethanol up to $x_{\text{TFE}} \approx 0.5$ is, however, practicable. The rate coefficient for TFE as solvent was obtained by plotting log k for reactions in TFE–ethanol mixtures *versus* x_{TFE} and extrapolating to $x_{\text{TFE}} = 1.00$. At $x_{\text{TFE}} \approx 0.5$ there were slight indications of a falling-away from a rectilinear plot, as would be expected from the results of other experiments on mixtures of two alcohols that differ markedly in polarity. A slight curvilinear relationship between log k and x_{TFE} was therefore assumed in the extrapolation. Thus our value of k for reaction in TFE must be regarded as only a very rough estimate.

Further, it must be stated that the results for certain of the electronegatively substituted alcohols were not highly reproducible. This was notably so for nos. 29—32, and some of these solvents also showed an appreciable but variable spontaneous reaction with DDM. Procedures were adopted to minimise these problems (see Experimental section), but the values of k were only reproducible to within about ±8%. This is to be compared with the ±2% reproducibility that we normally achieve in work on the reactions of DDM with carboxylic acids in alcohols. We also point out that experimental values are not available for the dielectric constants of four of these solvents, and in these instances values have been estimated from those of related compounds.

Because of these limitations of the data in Table 3, we do not immediately seek to incorporate nos. 28—36 in a new multiple regression, but rather to use the solvent parameters, in association with equation (2), to predict log k values for comparison with log k(obs.), as shown in Table 4. Bearing in mind the considerable extrapolation involved both in measuring k and in applying equation (2) for solvent no. 28 (TFE), the very good agreement between log k(obs.) and log k(pred.) for this solvent should not be over-emphasised. It is, however, satisfactory that log k for the reaction in TFE is certainly approximately as predicted from equation (2).

The agreement between log k(obs.) and log k(pred.) may also be considered satisfactory for nos. 32—34, bearing in mind the poor precision of the rate coefficient for no. 32 and the reliance on an estimated dielectric constant for no. 34. Varying the latter by ±3 would alter log k(pred.) by *ca.* ±0.06. (Further, the percentage purity of solvent 34 and the residual water contant of 32 did not achieve the levels we normally regard as acceptable. See Experimental section.)

For solvents 29—31 the agreement between log k(obs.) and log k(pred.) is not so satisfactory, but here we must again recall the poor precision of the rate coefficients and the use of estimated dielectric constants for nos. 30 and 31, although varying these by ±5 alters log k(pred.) by only about ±0.03.

The major discrepancies between log k(obs.) and log k(calc.) occur with nos. 35 (2-methoxyethanol) and 36 (2-phenoxyethanol), for which the rate coefficients were highly reproducible. [Varying the estimated dielectric constant of no. 36 by ±5 would change log k(pred.) by *ca.* ±0.07.] There is no doubt that the reactions in these solvents are very much slower than predicted, particularly for 2-methoxyethanol. It has been pointed out in earlier work [6] that the rate coefficients for reactions of DDM with carboxylic acids in 2-methoxyethanol are always comparable with the values for secondary alcohols as solvents, as if σ^* for MeO(CH$_2$)$_2$ were effectively *ca.* −0.2 instead of +0.19. It was then [6] suggested that the anomaly was connected with the special possibilities of hydrogen bonding involving Me*O* and *H*O that this solvent presents. This is supported by i.r. studies,[10] which indicate an equilibrium between three species: (i) non-hydrogen-bonded free monomer, (ii) an intramolecularly hydrogen-bonded five-membered ring (I), and (iii) an intermolecularly hydrogen-bonded dimer (II). For the hydrogen-bonded species, Lewis acidity of O*H* will be reduced and Lewis basicity of *O*H will be enhanced. In the solvent effect on the DDM reaction this will be equivalent to making σ^* rather more negative.

Similar hydrogen bonding will presumably occur for 2-

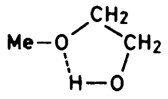
Table 3. Rate coefficients (l mol^{-1} min^{-1}) for the reaction between diazodiphenylmethane and benzoic acid in electronegatively substituted alcohols at 30.0 °C

No.	Solvent	k	ε [c]	σ^* [d]	$n_{\gamma H}$ [e]
28	2,2,2-Trifluoroethanol	1 620 [a]	26.1	0.92	0
29	2-Chloroethanol	24.9 [b]	25.8	0.385	0
30	2-Cyanoethanol	26.2 [b]	25	0.46	0
31	3-Chloropropan-1-ol	12.6 [b]	20	0.14	2
32	Ethane-1,2-diol	8.6 [b]	38.7	0.20	0
33	Propane-1,3-diol	5.5	35.0	0.07	2
34	4-Methoxybenzyl alcohol	4.4	12	0.14	0
35	2-Methoxyethanol	0.65 [f]	15.95	0.19	0
36	2-Phenoxyethanol	4.86	15	0.30	0

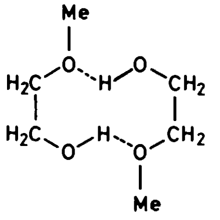
[a] By extrapolation from values for mixtures with ethanol (see text and Experimental section). [b] Reproducibility ±8% (see text and Experimental section). [c] Dielectric constant: nos. 28 and 29, 25 °C; nos. 32 and 33, 20 °C; no. 35, 30 °C; nos. 30, 31, 34, and 36, estimated from values for related compounds. [d] Polar substituent constant of XCH_2, from ref. 9, or estimated from values for related groups by applying CH_2 decremental factor, 2.8. No. 34 from C. Hansch and A. J. Leo, 'Substituent Constants for Correlation Analysis in Chemistry and Biology,' Wiley, New York, 1979. [e] Number of γ-hydrogen atoms. [f] Ref. 6.

Table 4. Comparison of log k(obs.) and log k(pred.) [from equation (2)] for reactions between diazodiphenylmethane and benzoic acid in electronegatively substituted alcohols

No.	Solvent	log k(obs.)	log k(pred.)
28	2,2,2-Trifluoroethanol	3.210	3.239
29	2-Chloroethanol	1.396	1.565
30	2-Cyanoethanol	1.418	1.799
31	3-Chloropropanol	1.100	0.862
32	Ethane-1,2-diol	0.935	1.025
33	Propane-1,3-diol	0.740	0.704
34	4-Methoxybenzyl alcohol	0.644	0.683
35	2-Methoxyethanol	−0.187	0.892
36	2-Phenoxyethanol	0.687	1.229



(I)



(II)

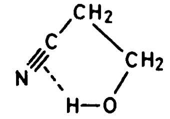
phenoxy-ethanol, but this will be less pronounced due to the delocalization of the electrons of the phenoxy *O* into the benzene ring. Thus the discrepancy between log k(obs.) and log k(pred.) is understandably reduced.

We now incorporate the electronegatively substituted alcohols in a new multiple regression, but omit nos. 35 and 36. Thus for nos. 1—34:

$$\log k = -1.486 + 3.892f(\varepsilon) + 2.990\sigma^* + 0.046n_{\gamma H} \quad (\pm0.556)\ (\pm0.078)\ (\pm0.007) \qquad (3)$$

$$n = 34 \qquad R = 0.993 \qquad s = 0.096$$

Comparison with equation (2) finds only slight changes in the values of regression coefficients. As a summary of the data, as indicated by s, equation (3) is somewhat inferior to (2), but the range of data incorporated in (3) is very much greater, and the R value is slightly increased. The effect of including the alcohols of highly positive σ* value (particularly TFE) is very noticeable in the stepwise regression. Simple regression of log k on σ* gives $r = 0.977$, and regression on σ* and f(ε) gives $R = 0.983$. The partial correlation coefficients in the stepwise regression are 0.51 and 0.77, significant at the 99.8 and >99.9% levels, respectively.



(III)

In view of the uncertainty in the rate coefficient for no. 28 (TFE) we give also the regression equation for nos. 1—27 and 29—34. The lower multiple correlation coefficient for equation

$$\log k = -1.565 + 4.057f(\varepsilon) + 2.869\sigma^* + 0.044n_{\gamma H} \quad (\pm0.549)\ (\pm0.105)\ (\pm0.007) \qquad (4)$$

$$n = 33 \qquad R = 0.988 \qquad s = 0.093$$

(4) compared with (3) is mainly due to the exclusion of the extreme value of log k for TFE.

The conformity of the data for solvents 30 and 31 to both equations (3) and (4) is rather poor, although that of 29 is acceptable. Thus the deviant behaviour of 2-cyanoethanol and 3-chloropropan-1-ol noted above for the predictions from equation (2) continues even when the data are allowed to influence the regressions in (3) and (4). The reaction in 2-cyanoethanol is *ca.* 0.25 log k units slower than given by equation (4), while that in 3-chloropropan-1-ol is *ca.* 0.3 units faster. It seems possible that the negative deviation shown by 2-cyanoethanol is due to hydrogen bonding, for which there is some spectroscopic evidence,[11] *e.g.* (III). Internal hydrogen bonding could conceivably occur in 3-chloropropan-1-ol, but spectroscopic evidence is against this [12] and it would not account for a positive deviation from the regression. There is no obvious explanation of this deviation.

In view of the deviations shown by solvents 30 and 31, and the extremely deviant behaviour of 35 and 36 discussed above, the conformity of the two diols, nos. 32 and 33, is remarkable. Deviations owing to hydrogen bonding (inter- or intra-molecular) might well have been expected.

Experimental

Materials.—Pure benzoic acid was available from earlier work.[6] Diazodiphenylmethane, prepared by the method of

Schroeder and Katz,[13] was stored over potassium hydroxide in a desiccator in a refrigerator.

As far as possible the solvents were purified along the lines used in earlier work,[6] *e.g.*, drying over K_2CO_3 and/or molecular sieve, followed by fractional distillation in nitrogen and sometimes under reduced pressure. Purity was monitored by g.l.c. and by Karl Fischer titration [14] for residual water. Solvents were stored and manipulated under dry nitrogen. The above procedure was essentially followed for 2-methybutan-1-ol, 2,2,2-trifluoroethanol, and propane-1,3-diol. For these solvents purity by g.l.c. was between 97 and 100%, and residual water was <0.02%. Ethanol was purified by Smith's method.[15]

Certain solvents were available as good commercial samples, whose purity by g.l.c. was adequate (98—100%) and whose residual water by Karl Fischer titration (carried out when the solvent was available in sufficient amount) was <0.02%. In this category were 3,3-dimethylbutan-2-ol, 2,3-dimethylbutan-2-ol, and 2-phenoxyethanol.

2,2-Dimethylpropan-1-ol (neopentyl alcohol), m.p. 52 °C, was purified by sublimation and contained no significant impurities by g.l.c.

Commercial 4-methoxybenzyl alcohol was fractionated under reduced pressure (b.p. 138 °C at 20 mmHg) but the fractionated material still contained small amounts of several impurities and was *ca.* 92% pure by g.l.c. However, a DDM solution therein was very stable over several hours and gave very reproducible kinetics.

Ethane-1,2-diol was dried repeatedly over sodium sulphate and fractionated under reduced pressure (b.p. 96 °C at 22 mmHg). The purified solvent was 99.8% pure by g.l.c., but its residual water content could not be reduced below about 0.1%.

Commercial 2-cyanoethanol was very pure by g.l.c. but contained some impurity that reacted fairly rapidly with DDM. Attempts to remove this impurity and to dry the solvent by normal procedures resulted in the vigorous polymerisation of the material when it was later heated for distillation. It was found, however, that the reactive impurity was gradually suppressed when successive small amounts of DDM were added, and ultimately a DDM solution of sufficient stability could be obtained.

2-Chloroethanol was dried over K_2CO_3 and distilled under reduced pressure (b.p. 42 °C at 30 mmHg); purity by g.l.c. 99.6%, residual water <0.01%. 3-Chloropropan-1-ol was similarly treated (b.p. 66 °C at 20 mmHg). Both of these purified solvents were found to react fairly rapidly with DDM. When passed through an alumina column after distillation, the solvents gave more stable DDM solutions but the reactive impurity (probably HCl) reappeared on standing. It was therefore necessary to purify these solvents as indicated and to carry out the kinetic experiments without delay.

Kinetic Studies.—Adequate accounts of the general procedure for spectrophotometric determination of rate coefficients for the reactions of diazodiphenylmethane with benzoic acid have been given previously.[6] The first-order procedure was used with initial concentrations of acid and DDM of *ca.* 0.035 and 0.0035M, respectively, for the slower reactions and of *ca.* 0.007 and 0.0007M, respectively, for the faster reactions. As already indicated, some of the solvents presented difficulties for the kinetic studies and in such instances much repetition of measurements, frequently with fresh samples of solvent, was necessary. While the better behaved solvents gave reproducibility in k to within ±2%, as normally expected for DDM reactions, in the case of 2-chloroethanol, 2-cyanoethanol, 3-chloropropan-1-ol, and ethane-1,2-diol the reproducibility was to within about ±8%. For the first three solvents mentioned there was also a spontaneous reaction of the solvent with DDM. Because of its variability it was not possible to correct for this, but in no case did the spontaneous rate amount to more than *ca.* 5% of the total rate of consumption of DDM.

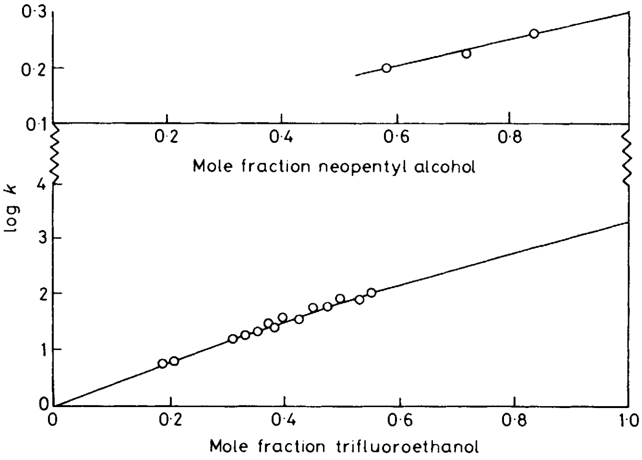


Figure. Rate coefficients for reaction of DDM with benzoic acid in mixtures of ethanol and neopentyl alcohol or trifluoroethanol at 30.0 °C

The notional rate constant for the reaction of DDM with benzoic acid in liquid neopentyl alcohol was determined by extrapolation of results for neopentyl alcohol–ethanol mixtures (see Figure). Many measurements of rate constants were made for reaction in TFE–ethanol mixtures of x_{TFE} up to *ca.* 0.5. Above this mole fraction the spontaneous consumption of DDM became very noticeable. The Figure shows detailed results and the form of the extrapolation to $x_{TFE} = 1.00$. A curvilinear relationship between log k and x_{TFE} would be expected from experiments with other mixtures of alcohols differing considerably in polarity. Clearly the value of k as determined for TFE can be regarded as only a very rough estimate.

Dielectric Constant Measurements.—The dielectric constants of 3,3-dimethylbutan-2-ol and 2,3-dimethylbutan-2-ol were measured by means of a simple bridge and liquid-containing cell with variable condenser. The values (19 °C) were found to be 4.55 and 3.63, respectively. The accuracy of the method was monitored by determining the dielectric constants of 2-methylbutan-2-ol and of cyclohexane. The values (20 °C) were 5.90 and 2.02, respectively, *cf.* 5.82 and 2.023, respectively.[16] This apparatus was not suitable for determining $\varepsilon > 7$. Attempts to measure, with more elaborate bridges, the dielectric constants of certain other solvents were unsuccessful owing to the appreciably conducting nature of the liquids involved.

Acknowledgements

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