A Quantum Chemical Treatment of the Basicities of the Methylbenzenes in the Ground and Lowest Triplet States[1a]

BY R. L. FLURRY, JR.,[1b] AND P. G. LYKOS

This work is part of an attempt to calculate "hyperconjugation" effects by a method which attributes no π-electronic character to the methyl group. The predicted basicities of the methylbenzenes in the ground and first excited triplet states are presented. In this work, the methyl substituent is considered to exert a purely inductive effect which manifests itself in a change in the 2p π-orbital exponent of the substituted carbon. The two-electron localization energies for the methylbenzenes in the ground and triplet states are calculated using a SCMO method. The energies so obtained for the ground state give good agreement with the observed basicity constants in liquid HF.[9] The spin densities calculated for the methylbenzene negative ions using the same parameters[6] also give good agreement with those observed. It is therefore felt that our predictions are valid for the excited state basicities. A comparison is made with the results of Ehrenson for both an electron de-localization[10] and an inductive treatment[5] of the methyl groups in calculating the ground state basicities.

Introduction

There have been various attempts to offer a theoretical explanation of the phenomena known as "hyperconjugation." The earliest attempt to calculate such effects employed an inductive effect which changed the Coulomb term, α, in the Hückel molecular orbital (HMO) description of the system.[2] Most subsequent treatments have assigned π-electronic character to the methyl groups, allowing delocalization of the methyl group electrons into the π-systems of attached conjugated systems.[3] It has also been suggested that the true effect is a combination of these two effects.[4,5] The present work is a continuation of our attempt to improve the inductive model and to apply it within the self-consistent molecular orbital (SCMO) formalism.[6]

The series of methylbenzenes, from benzene to hexamethylbenzene (thirteen molecules in all) offers a good test for any theoretical treatment of hyperconjugation. These compounds are found to be slightly basic in solvents of high acidity. The relative basicities of the series in liquid HF has been studied in three laboratories.[7–9] The three sets of results are in qualitative and semiquantitative agreement. The results of Mackor, *et al.*,[9] although encompassing only a part of the series, seem to have the greatest quantitative significance.

Ehrenson has performed theoretical calculations of the basicities of the series using a hyperconjugation model,[10] an inductive model[5] and a combination of the two.[5] The calculations employed the "ω-technique" of Wheland[11] and in the inductive model only the α-term for the substituted carbon was modified. His results gave good qualitative agreement for the entire series and fair quantitative agreement for part of the series.

Theory.—The nature of the protonated complex of a benzene ring has been the subject of much controversy. The bulk of the experimental evidence has been interpreted as the formation of a so-called "σ-complex," or "Wheland intermediate,"[12] for the structure of the complex.[13] In such a structure, the added proton causes a rehybridization of the position of attachment to give a tetrahedral center in the system. A recent spectroscopic study of the protonated methylbenzenes, however, indicates that, in this case at least, the intermediate may be a charge transfer complex.[14]

If the complex is an actual "Wheland intermediate," localization energy calculations which calculate the energy required to isolate completely a given center from the π-system of the molecule should give good correlation with the experimental basicities.

Brown[15] has proposed a reactivity index (called Z-value) for aromatic substitution which involves the assumption of a charge-transfer complex as the reaction intermediate. If the charge-transfer complex is the actual intermediate, the basicities should correlate well with Brown's Z-values. Unfortunately, however, these two methods of calculation cannot be used to distinguish between the possible forms of the complex, since Brown's Z-values can be correlated through Fukui's superdelocalizabilities[16] to localization energies.[17] Since either type of complex should, therefore, correlate with localization energies, that reactivity index was used in the present calculations because of convenience.

The two-electron localization energies were obtained from the differences in energy of the parent compound and the pentadienyl cation which remains when two electrons are localized on a center. These energies were related to the equilibrium constants by use of eq. 1,

$$-RT \ln K/K_s = \Delta E - \Delta E_s \qquad (1)$$

which employs the usual assumption of proportionality of ΔE and ΔF used in calculations of this type.[18] The subscript, s, refers to a standard compound in the series to which the other members are compared. Since, in this work, the methyl-substituted carbon was treated as a hetero atom, a separate standard was chosen for substitution at a methyl-bearing and at a non-methyl-bearing position.[19] The values reported here follow the lead of McCaulay and Lien[7] in referring all the basicities to *p*-xylene.

Calculations.—The method of choosing the parameters which were employed has been discussed in

(1) (a) Presented by R. L. F. at the 142nd National Meeting, Am. Chem. Soc., Atlantic City, N. J., September, 1962. (b) National Institutes of Health Postdoctoral Fellow, 1961–1962.

(2) G. W. Wheland and L. Pauling, *J. Am. Chem. Soc.*, **57**, 2086 (1935).

(3) R. S. Mulliken, *J. Chem. Phys.*, **7**, 339 (1939); A. Streitwieser, Jr., and P. M. Nair, *Tetrahedron*, **5**, 149 (1959).

(4) R. W. Taft and I. C. Lewis, *ibid.*, **5**, 210 (1959).

(5) S. Ehrenson, *J. Am. Chem. Soc.*, **84**, 2681 (1962).

(6) R. L. Flurry, Jr., and P. G. Lykos, *Mol. Phys.*, in press.

(7) D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.*, **73**, 2013 (1951).

(8) M. Kilpatrick and F. E. Luborsky, *ibid.*, **75**, 577 (1953).

(9) E. L. Mackor, A. Hofstra and J. H. van der Waals, *Trans. Faraday Soc.*, **54**, 186 (1958).

(10) S. Ehrenson, *J. Am. Chem. Soc.*, **83**, 4493 (1961).

(11) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).

(12) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).

(13) C. MacLean, J. H. van der Waals and E. L. Mackor, *Mol. Phys.*, **1**, 247 (1958).

(14) R. L. Flurry, Jr., and J. G. Jones, to be published.

(15) (a) R. D. Brown, *J. Chem. Soc.*, 2224 (1959); (b) *ibid.*, 2232 (1959).

(16) K. Fukui, K. Morkuma, T. Youezawa and C. Nagata, *J. Chem. Phys.*, **32**, 1743 (1960).

(17) J. Koutecký, R. Zahradník and J. Čížek, *Trans. Faraday Soc.*, **57**, 169 (1961).

(18) R. Daudel, R. Lefebvre and C. Moser, "Quantum Chemistry," Interscience Publishers, Inc., New York, N. Y., 1959, p. 269.

(19) The necessity for this stems from an inherent weakness of the Wheland localization energy as generally employed in π-electron calculations. The actual localization energy should be the sum of the energies of the pentadienyl fragment and of the removed fragment with the localized electrons in its π-orbital. This second term is dependent on the nature of the removed center. Only if all centers are identical can a direct comparison be made without regard to the energy of the removed fragment.

TABLE I

GROUND STATE EQUILIBRIUM CONSTANTS

| Hydrocarbon[a] | This work | Calculated log K/K_s | | | Experimental K/K_s | | |
		H.C.[b]	Ehrenson In.[c]	C.[d]	Mackor[e]	McCaulay[f]	Kilpatrick[g]
Benzene [1]	−3.75	−2.40	−3.0	−4.0–3.7	−3.7	...	−1.0
Toluene (1) [2]	−0.64	−0.50	−1.1	−0.96–0.89	−0.6	−2.0	−0.20
p-Xylene (1,4) [1]	0	0	0	0	0	0	0
o-Xylene (1,2) [1]	+0.67	0.11	0.26	0.26	...	0.30	0.04
m-Xylene (1,3) [2]	2.60	1.53	1.0	1.9–2.0	2.5	1.3	1.4
Pseudocumene (1,2,4) [3]	3.06	1.62	1.7	2.0–2.1	...	1.6	1.8
Hemimellitene (1,2,3) [2]	3.09	1.72	2.0	2.3–2.5	...	1.6	1.8
Durene (1,2,4,5) [3]	3.92	1.99	2.5	2.7–2.9	...	2.1	2.1
Prehnitene (1,2,3,4) [2]	3.50	2.26	3.0	2.9–3.2	...	2.2	2.6
Mesitylene (1,3,5) [2]	5.21	3.28	2.8	4.3–4.6	5.3	3.4	4.1
Isodurene (1,2,3,5) [4]	5.56	3.34	3.7	4.8–5.0	...	3.8	4.2
Pentamethylbenzene (1,2,3,4,5) [6]	5.65	3.48	4.4	5.0–5.4	...	3.9	4.5
Hexamethylbenzene [1]	6.67	4.04	5.2	5.8–6.2	7.1	4.9	5.0

[a] Position of methyl substitution shown in parentheses, position of protonation in brackets. [b] Hyperconjugation model, ref. 10. [c] Inductive model, ref. 5. [d] Combination of hyperconjugation and inductive, ref. 5. [e] Ref. 9. [f] Ref. 7. [g] Ref. 8.

detail previously[6]; therefore, only the essentials of the method will be presented here.

From a study of the virial theorem within the π-electron approximation,[20] we have shown that for a single π-type center, assuming a Slater-type orbital (STO) on the central atom and the validity of Koopmans' theorem, the change in the ionization potential on successive substitution by a substituent which exerts only an inductive effect may be expressed as

$$I^0 - I^{(n)} = \frac{(n\delta\zeta)^2}{2} - nK \qquad (2)$$

where I^0 is the ionization potential of an electron in the π-atomic orbital, $I^{(n)}$ is the corresponding ionization potential when n identical inductive groups are attached, n is the number of such groups, $\delta\zeta$ is the change in the orbital exponent of the STO and K is a constant containing various electron interaction terms. Applying this relationship to the ionization potentials of the series methyl radical to tert-butyl radical, a best value of 0.1106 is obtained for $\delta\zeta$.[21]

A simplified form of the SCMO equation for a closed shell system[22] is shown in eq. 3.

$$E_n = \sum_i C_{in}^2\alpha_i + 2\Sigma_{i>j} p_{ij}\beta_{ij} \qquad (3)$$

where

$$\alpha_i = (\alpha_i)_{core} + \frac{1}{2}q_i(ii/ii) + \sum_{j \neq i} q_j(ii/jj)$$

$$\beta_{ij} = (\beta_{ij})_{core} - \frac{1}{2}p_{ij}(ii/jj)$$

The modification of the orbital exponent allows for three changes in the SCMO computational scheme. First, the α-term of the core matrix is modified by using the $(11|11)$ integral adjusted for the change in the STO orbital exponent and by modifying the W_{2p} accordingly within the Goeppert-Mayer and Sklar expansion. The second change occurs in the two-center integrals which involve the substituted center. These are evaluated theoretically using the appropriate STO's. Finally, the β-terms of the core matrix are assumed to be proportional to overlap and are modified by the introduction of the modified orbital exponent. The last two changes have been neglected in previous calculations employing an inductive effect.[5]

The calculations were performed on a Univac 1105 digital computer using a modification of Roothaan's SCMO methods[23] for both closed and open shell sys-

tems. A single configuration wave function was used which was formed from molecular orbitals represented as linear combinations of atomic orbitals. The original parameters were taken from Pritchard and Skinner's valence state ionization potentials[24] and from Pariser and Parr's expansion for β.[25] All molecules were assumed to be regular hexagons with bond lengths equal to those of benzene.

The correlation of the calculated localization energies was obtained by a least squares fit of log K/K_s vs. $(\Delta E_s - \Delta E)$ for Mackor's data for toluene, m-xylene and mesitylene. The slope obtained was 346.9 a.u.$^{-1}$ (1 a.u. = 27.21 e.v.). If the equality in eq. 1 were exact, the theoretical slope at 0° should be 502.3 a.u. This implies a modification of eq. 1 to give eq. 4

$$-(2.303)RT \log (K/K_s) = \mu(\Delta E - \Delta E_s) \qquad (4)$$

where μ is a proportionality constant which equals 0.69 in this case.

Corrections were made for the number of equivalent reactive sites in all cases.

Results

A. Ground State Basicities.—In Table I are presented our results for the ground state basicities along with the three sets of experimental results and Ehrenson's results.[5,10] As can be seen, there is qualitative agreement among all sets of work, with the exception of mesitylene in Ehrenson's inductive model. The values calculated in the present work give excellent quantitative agreement with the results of Mackor, et al.[26] The hyperconjugation results of Ehrenson can be improved considerably with respect to Mackor's data by multiplying each of the values by 1.60. The results for the higher members in the combination model can be improved by multiplying the larger numbers in the reported range by 1.15. No constant multiplicative factor can improve the simple inductive model; however, they can be considerably improved by taking cognizance of the effect commented on in footnote 19. These results indicate that a refined inductive treatment as used here is better than the simple inductive model which has been previously used. It also appears to be somewhat better than the hyperconjugation model or the combined model as employed by Ehrenson if the experimental data of Mackor are accepted as the most reliable.

B. Triplet State Basicities.—The agreement of the calculated results with the ground state basicities is

(20) R. L. Flurry, Jr., and P. G. Lykos, to be published.
(21) $\delta\zeta$ is a scale factor, and actually scales the best distorted π-orbital, whatever its explicit form might be (see R. L. Miller and P. G. Lykos, J. Chem. Phys., **37**, 993 (1962).
(22) J. A. Pople, Trans. Faraday Soc., **49**, 1375 (1953).
(23) C. C. J. Roothaan, Rev. Mod. Phys., **32**, 179 (1960).

(24) H. O. Pritchard and H. A. Skinner, Chem. Rev., **55**, 745 (1955).
(25) R. Pariser and R. G. Parr, J. Chem. Phys., **21**, 767 (1953).
(26) The small discrepancy in the case of hexamethylbenzene is expected owing to the steric crowding of the six methyl groups around the ring.

excellent. The agreement of the previously reported spin densities of the methylbenzene negative ions[6] with available experimental data is also quite good. The latter series involved direct calculations of doublet states (which in general, are quite perturbed) of the molecules in question using the open shell SCMO procedure. In view of the success of these two calculations, it is felt that our calculations of the triplet state basicities will be valid.

In the triplet state calculations, the ΔE values for use in eq. 4 were taken as the differences in the π-electronic energies of the parent molecule and the remaining pentadienyl cation fragment in their triplet states,[27,28] including the correction for protonation at a methyl-bearing site.

The predicted triplet state basicities are reported in Table II, both with reference to the p-xylene triplet

TABLE II
CALCULATED TRIPLET STATE EQUILIBRIUM CONSTANTS

Hydrocarbon[a]	Log K/K_s[b]	Log K^c
Benzene [1]	−11.64	23.64
Toluene (1) [3]	−9.32	25.96
m-Xylene (1,3) [5]	−4.17	31.11
Hemimellitene (1,2,3) [1]	−3.84	31.44
Prehnitene (1,2,3,4) [5]	−2.31	32.97
Mesitylene (1,3,5) [1]	−1.91	33.37
Isodurene (1,2,3,5) [4]	−1.61	33.67
p-Xylene (1,4) [1]	0	35.28
o-Xylene (1,2) [1]	+0.92	36.20
Durene (1,2,4,5) [3]	1.24	36.52
Pseudocumene (1,2,4) [6]	+2.40	37.68
Pentamethylbenzene (1,2,3,4,5) [1]	2.97	38.25
Hexamethylbenzene [1]	3.10	38.38

[a] See footnote a, Table I. [b] Relative to the p-xylene triplet state basicity. [c] Absolute values relative to the ground state values from ref. 9.

state basicity, and as absolute values referred to the absolute values quoted by Mackor.[9] If the absolute basicities are valid, these compounds should all be respectable bases in aqueous solutions when they are in their lowest ($\pi \rightarrow \pi^*$) triplet states.

Discussion

In order to assess the validity of the present inductive model for ground state basicities, a critical comparison with the inductive and hyperconjugative results of Ehrenson is desirable. Figure 1 presents a plot of the calculated logarithms of the basicity constants from references 5 and 10 vs. the experimental values from reference 9. It is seen that except for hexamethylbenzene (h.m.b.) the results of the hyperconjugation calculation give a good linear correlation. The slope, however, is not unity. (This was noted and commented on in reference 10.) These may be brought into line by multiplying all values by a constant value of 1.60. (This is equivalent to a μ value of 1.60 in eq. 4.) The value of 1.60 for μ is needed to convert McCaulay's experimental values to the same scale that Mackor used. Since Ehrenson calibrated his parameters to give agreement with McCaulay's experimental values, the same proportionality constant would correlate his calculated values to Mackor's experimental values. Since our parameter values are inferred from spectroscopic data there need not be a one-to-one correspondence between our values and Ehrenson's.

(27) For a discussion of the multiplicity requirements in excited state reactions, see K. Fukui, K. Morokuma and T. Yonezawa, *Bull. Chem. Soc. Japan*, **34**, 1178 (1961).

(28) It should be emphasized that these are calculations performed directly on the triplet state using an open shell SCMO procedure, and not based on the virtual orbitals obtained from ground state calculations.
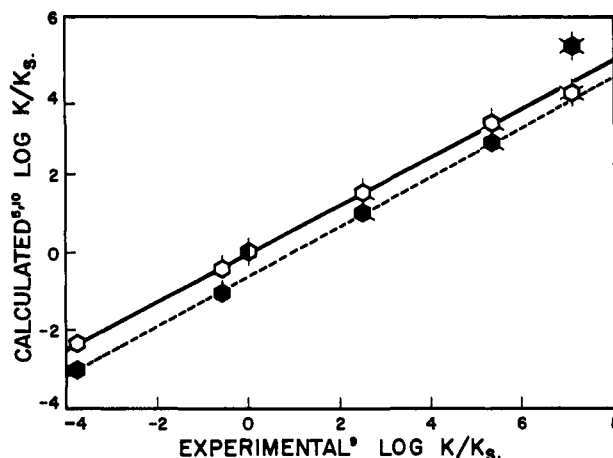

Fig. 1.—Plot of calculated vs. experimental[9] log K/K_s for hyperconjugative[10] (open figures) and simple inductive[5] (black figures) models.

Ehrenson's inductive values give a linear correlation for the molecules benzene, toluene, m-xylene and mesitylene, but not for p-xylene and h.m.b. In his calculations, however, Ehrenson assumes that the localization energy correlation is independent of the type of position protonated. If a constant (−0.7) is added to the values for p-xylene and h.m.b.[19] (both of which have a methyl-substituted position as the most reactive), the correlation is made linear. A μ-value of 1.55 now produces agreement with experiment. The corrected inductive and hyperconjugative basicities are presented in Table III along with the result from the present work and the experimental results.

TABLE III
CORRECTED GROUND STATE BASICITIES[a]

Compound	Corrected H.C.[b]	Values In.[c]	This work	Experimental, ref. 9
Benzene	−3.8	−3.6	−3.7	−3.7
Toluene	−0.8	−0.6	−0.6	−0.6
p-Xylene	0	0	0	0
m-Xylene	2.3	2.6	2.6	2.5
Mesitylene	5.1	5.4	5.2	5.4
Hexamethylbenzene	6.4	8.1	6.7	7.1
Average deviation	10.5%	3.5%	2.2%	

[a] See text. [b] Hyperconjugation, ref. 10. [c] Inductive, ref. 5.

After correction, the simple inductive treatment gives almost as good agreement with experiment as does the more refined inductive treatment. These results lead to the conclusion that the inductive model indeed leads to a valid method for calculating reactivities of methyl-substituted π-electron systems.

The excellent success of the ground state basicity calculations lends credulence to the values for the predicted triplet state basicities. Some comments about these are in order, however.

The approximation expressed in eq. 1 assumes a constant entropy change to be involved in the formation of the protonated complexes of the series.[29] There is no reason to assume, however, that this constant entropy change should carry over from the ground state protonation to the excited state protonation, especially when a change of multiplicity is involved. Therefore no faith can be placed in the absolute value of basicities reported. On the other hand, the triplet states

(29) The fact that a μ-factor must be introduced to achieve correlation with experiment (eq. 4) indicates either that the entropy change is not constant, but rather is proportional to the energy change, or that the localization energy as calculated represents a false description of the excitation to the protonated complex.

can be expected to be considerably more basic than the ground state molecules[30] and the relative magnitudes of the basicities should be valid.

It is of interest to compare the predicted position of protonation in the ground and triplet states of the various molecules. It is seen that, in most cases, this has changed in the excited state, usually going to the position which is least active in the ground state. This is a consequence of the intramolecular charge transfer on excitation to a higher energy state.[31]

The relative basicities within the series are also interesting. It is seen that in every case where there is more than one methyl-substituted isomer (the di-, tri- and tetramethylbenzenes) the most basic and least basic members of the group exchanged relative position. In the case of the tetramethylbenzenes there was a complete reversal of order. Thus this series of molecules constitutes an example of the intramolecular charge-transfer phenomenon which occurs on excitation together with its attendant profound influence on the

(30) In order to bring the triplet state basicities in line with those of the ground state, an entropy difference of greater than 100 e.u. at 0° for reaction in the different states would be required. It is unlikely that even the solvation changes which would be expected to accompany the electronic reorganization could cause such an entropy change.

(31) For a graphic discussion of such effects in small systems see M. Kasha in "Comparative Effects of Radiation," John Wiley and Sons, Inc., New York, N. Y., 1960, p. 72.

relative reactivities of the unique position in each molecule as well as on the series itself.

Conclusion

A refined inductive treatment of methyl-substituted π-electronic systems has been presented and applied to the calculation of the basicities of the methyl-substituted benzenes. When the localization energy approximation was corrected to allow for different type centers in the molecules, the agreement with experiment for ground state basicities was excellent. Basicities for these molecules in their first excited triplet state were also predicted.

It was shown that by application of a correction to the localization energies, Ehrenson's inductive results, which used a simpler model, could be improved to give good agreement with experiment.

It is anticipated that the method of calculation and the methyl group inductive parameters employed in this work can be used to predict correctly reactivities and other properties of other systems, including those which have methyl substitution on heteroatoms.

Kinetics of Hydrolysis of Acetals in Protium and Deuterium Oxides[1]

BY MARTIN KILPATRICK

The acid-catalyzed hydrolysis of ethylene acetal (2-methyl-1,3-dioxolane) and dimethyl acetal (1,1-dimethoxyethane) has been studied over the temperature range 0–40°. The experimental results can be represented within the experimental accuracy by a two-parameter Arrhenius equation and the ratio of the velocity constants in deuterium oxide to protium oxide is dependent on the difference in the energies of activation. The ratio $k_{H_2O}^{DCl}/k_{H_2O}^{HCl}$ decreases with increasing temperature for both acetals and is in qualitative agreement with theoretical calculations.

In 1940, Kilpatrick and Riesch[2] reported briefly that the experimental energy of activation for the hydrolysis of acetals for the temperature range 0–40° varied with temperature, the decrease with increasing temperature being −33 calories per degree for diethyl acetal, −7 calories per degree for ethylene acetal and essentially zero for dimethyl acetal. Changing the medium by the addition of salts did not appreciably change the experimentally determined energy of activation, although the electrolyte effect on the rate was of considerable magnitude. The sensitivity of these reactions to hydrogen ion varies in the ratio 1:20:100 for ethylene, dimethyl and diethyl acetals so that at 0° one can obtain accurate second-order constants by the dilatometric method up to 0.01 M HCl for diethyl, 0.1 for dimethyl and 1.0 for ethylene acetal. At 40° the convenient concentration of strong acids is reduced by a factor of 200 and directly determined velocity constants are less reliable owing to the basicity of the acetal or to acidic impurities. By using the two-thermostat method and assuming the pre-exponential factor in the Arrhenius equation to be constant over a temperature interval, experimental energies of activation can be determined without an accurate knowledge of the hydrogen ion concentration.

(1) Based on work performed in part under the auspices of the U. S. Atomic Energy Commission.

(2) M. Kilpatrick and L. C. Riesch, "Handbuch der Katalyse," Vol. 1, Julius Springer, Vienna, Austria, 1940, p. 258.

Earlier experiments were also attempted in the solvent D_2O by microdilatometric and interferometric techniques, but the limited supply of deuterium oxide prevented the completion of sufficient accurate determinations for publication. The ample supply of D_2O at the Argonne Laboratories has afforded an opportunity to complete this work on a macro scale and the results are reported here. A limited number of experiments has also been carried out at 25° spectrophotometrically as a check on the reliability of the dilatometric method.

Experimental

Ethylene acetal was prepared from acetaldehyde and ethylene glycol in the presence of $CaCl_2$, the upper layer separated and washed with a saturated solution of calcium chloride and dried over $CaCl_2$. After further drying with K_2CO_3 to prevent acid-catalyzed decomposition, the product was distilled and finally fractionated and the fraction boiling between 82.5 and 83.0° at 760 mm. was used for the measurements.

Dimethyl acetal was purified by fractional distillation of commercial samples after treating with K_2CO_3 and that fraction distilling between 63.5 and 64.0° at 760 mm. was used.

Various preparations of acetals were used in the course of the work and all gave kinetic results agreeing within 2%. The samples were tested periodically for acidity by adding 0.5 ml. to 50 ml. of carbon dioxide-free water containing brom thymol blue.

In some cases the acetals were tested on the vapor phase chromatograph and found to be better than 99% pure. The purity was also checked for decomposition by ultraviolet absorption measurements for acetaldehyde, the decomposition product. During the course of the work it was found necessary to keep the