ELECTRIC MOMENTS OF SOME METHYL KETONES

A THESIS

IN CHEMISTRY

by

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Approved

Texas Technological College

May, 1953

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**A THESIS
IN CHEMISTRY**

**Submitted to the Faculty of the Division of
Graduate Studies of Texas Technological College
in Partial Fulfillment of the Requirements
for the Degree of**

MASTER OF SCIENCE

by

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May, 1953

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Acknowledgement

The author expresses gratitude to Dr. George K. Estok for collaboration in constructing the apparatus used, and for furnishing two of the ketones used. His advice and assistance were invaluable.

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STATEMENT OF THE PROBLEM

The problem consisted of the determination of the electric moments of several unsaturated and saturated aliphatic methyl ketones in benzene and 1,4-dioxane solutions, and the interpretation of the values in terms of resonance, methyl group hyperconjugation, preferred molecular configurations, and solvent effects.

INTRODUCTION

The results of electric moment determinations, when properly interpreted, frequently furnish knowledge of structures of molecules. Information concerning distributions of electronic fields, molecular configurations, and the effects of resonance can often be obtained by electric moment studies.

In many instances resonance structures involving hyperconjugated methyl groups have been postulated to account for certain molecular properties. A classical example is the ortho-para-directing influence of the methyl group in toluene, which is attributed to contributions from resonance structures such as:

The influence of resonance and hyperconjugated methyl groups on the electric moments of some aliphatic compounds is shown by the instances given in Table I, with appropriate literature references.

A general discussion of resonance and electric moments is given by Smyth in "Chemical Architecture"¹.

Table I
Electric Moments and
Effects of Methyl Hyperconjugation

<u>Hydrocarbons:</u>	Formula	Method	Moment	Reference
ethylene	$\text{H}_2\text{C}=\text{CH}_2$	gas	0	(2)
propylene	$\text{CH}_3\text{CH}=\text{CH}_2$	gas	0.35 D	(3)
methylacetylene	$\text{CH}_3\text{CH}\equiv\text{CH}$	gas	0.77	(4)
<u>Aldehydes:</u>				
acrolein	$\text{CH}_2=\text{CH}-\text{CHO}$	benzene	2.90	(5)
methacrolein	$\text{CH}_2=\text{C}-\text{CHO}$ CH_3	benzene	2.72	(6)
crotonaldehyde	$\text{CH}_3\text{CH}=\text{CH}-\text{CHO}$	CCl_4	3.54	(5)
tiglaldehyde	$\text{CH}_3\text{CH}=\text{C}-\text{CHO}$ CH_3	benzene	3.39	(6)
<u>Nitriles:</u>				
acrylonitrile	$\text{CH}_2=\text{CH}-\text{CN}$	gas	3.88	(7)
methacrylo- nitrile	$\text{CH}_2=\text{C}-\text{CN}$ CH_3	gas	3.69	(8)

The symmetry of the ethylene molecule accounts for its zero moment. The moment of 0.35D for propylene is attributed to contributions from hyperconjugated resonance structures such as $\overset{+}{\text{H}} \text{CH}_2=\text{CH}-\overset{-}{\text{CH}_2}$. This structure is in agreement with the directive influence predicted by Markownikoff's addition rule relating to unsymmetrical olefins. The higher moment of 0.77 for methylacetylene can be attributed to considerable contribution from

hyperconjugated structures such as $\text{H}^+ \text{CH}_2 = \text{C} = \text{CH}^-$.

Considering the aldehydes in Table I, the high moment of 2.90 for acrolein shows the influence of the resonance structure $\text{H}_2\text{C}^+ - \text{CH} = \text{CH} - \text{O}^-$ on the total moment. The carbonyl group moment, as illustrated by the moment of acetaldehyde or propionaldehyde, is only of the general magnitude 2.7 D. The additional presence of an alpha-methyl group results in a decrease in moment from 2.90 for acrolein to 2.72 for methacrolein. Therefore, in this case, the alpha-methyl group hyperconjugates in opposition to the main moment and effectively cancels the contribution of resonance of the type shown for acrolein.

The effect of the alpha-methyl group in reducing moment is also observed by comparing the moments of crotonaldehyde, 3.54, and tiglaldehyde, 3.39. Comparison of the moments of acrylonitrile and methacrylonitrile further illustrate this effect.

Bentley, et al.⁵ determined moments on a number of unsaturated aldehydes and ketones of which mesityl oxide is of interest here. They determined a moment of 2.84 for this compound in benzene solution, a moment not a great deal higher than the average value of about 2.75 for saturated aliphatic ketones. But in a rather analogous case, crotonaldehyde has a high moment of 3.54 (Table I) as compared to a value of about 2.7 for saturated aliphatic aldehydes.

An explanation of this appreciable difference between the moments of mesityl oxide and crotonaldehyde is found in the existence of so called "single-bond cis-trans isomerism."⁹ This condition can exist when resonance causes partial double bond character in bonds which are ordinarily written as single bonds. Thus in conjugated unsaturated carbonyl compounds resonance places partial double bond character between the alpha and carbonyl carbon atoms.

From this partial double bond character result two preferred configurations which can accommodate it, the single-bond (s-cis) and the single-bond trans (s-trans) forms. In the former it is noted that the moment (μ_2) due to the resonance structure does not contribute greatly to the main carbonyl moment (μ_1). Thus mesityl oxide is said to have predominantly the s-cis configuration which accounts for its rather low moment, while crotonaldehyde has predominantly the s-trans configuration in which the resonance structure contributes greatly to the total electric moment.

Curran and Estok¹⁰ have reported the influence of solvent on contributions made by polar resonance structures for the case of anilines substituted in the para positions by electron withdrawing groups. These solutes always yielded higher apparent electric moments in dioxane than in benzene solutions; i.e., p-aminoacetophenone, 3.28 (in benzene) and 3.67 (in dioxane); p-nitroaniline, 6.31 and 6.88; p-aminobenzonitrile, 5.96 and 6.46, etc. The higher values in dioxane solutions were attributed to solute-solvent interaction in which highly polar resonance structures, such as $\text{H}_2\text{N}^+=\text{C}_6\text{H}_4=\text{C}=\text{N}^-$, are stabilized by hydrogen bonding between amino hydrogen and an oxygen atom of dioxane; i.e.,

The work reported in this thesis was carried out to study the effects of methyl group hyperconjugation, and other resonance, on the moments of certain unsaturated aliphatic methyl ketones. Information concerning molecular configurations of the s-cis and s-trans types was desired. Two saturated methyl ketones were also studied for comparative purposes. Moments for all except one of the ketones were determined in benzene and dioxane solutions to note possible solvent effects, particularly whether dioxane would stabilize a highly polar resonance structure involv-

ing methyl group hyperconjugation by electrostatically interacting with it as illustrated in the following:

EXPERIMENTAL

Preparation and Purification of Compounds

The boiling points for all reported compounds have been corrected to 760 mm. of mercury.

Mesityl oxide, an Eastman Kodak Company White Label product, was carefully fractionated through a metal helix packed column at reduced pressure, b.p. 129° , n_D^{25} : 1.4438, d_4^{25} : 0.8597.

Methylmesityl oxide (3,4-dimethyl-3-penten-2-one) was obtained at an earlier date by careful fractionation from the several products obtained by the acetylation of trimethylethylene with acetic anhydride in the presence of anhydrous zinc chloride¹¹. The compound was purified again by careful fractionation at reduced pressure just prior to use, b.p. 149° , n_D^{25} : 1.4500, d_4^{25} : 0.8704.

Methyl isopropenyl ketone (3-methyl-3-buten-2-one) was prepared by deaminating the product formed by the reaction of ethyl methyl ketone, formaldehyde, and dimethylamine hydrochloride, as reported by Hagemeyer¹². The product was carefully fractionated at reduced pressure, b.p. 98° , n_D^{25} : 1.4212. Insufficient yield was obtained to permit a density determination.

3,4-dimethyl-4-penten-2-one was obtained as one of the products from the same reaction which produced methylmesityl oxide, and was similarly purified, b.p. 131° , n_D^{25} : 1.4230, d_4^{25} : 0.8406. Work done by Yarze¹³ proved that this product was an unsaturated ketone with the same carbon skeleton as methylmesityl oxide; work by Lstok¹¹ confirmed the presence of the methylene group.

Methyl ethyl ketone, a Greene Brothers Company technical grade product, was carefully fractionated at atmospheric pressure, b.p. 79.5° , n_D^{25} : 1.3774, d_4^{25} : 0.8023.

Methyl isopropyl ketone, an Eastman Kodak Company highest purity product, was carefully fractionated just prior to use, b.p. 94° , n_D^{25} : 1.3860, d_4^{25} : 0.8000.

Benzene, an Eastman Kodak Company thiophene free product, was dried by refluxing it over phosphorus pentoxide. The material was then distilled through a large column packed with glass helices, the first 50 ml. portion of distillate being discarded. This method of purification was used earlier by Moede and Curran¹⁴.

1,4-Dioxane, an Eastman Kodak Company technical grade product, was purified and dried according to the method indicated by Fieser¹⁵. This method consists in refluxing the dioxane with hydrochloric acid for a considerable period, after which it is dried first with solid potassium hydroxide pellets and then a long reflux with metallic

sodium. The material was then distilled through a glass helix packed column, the first small portion of distillate being discarded.

Attempted Preparation of Ethylideneacetone (3-penten-2-one). Several attempts were made to prepare this compound but insufficient yields were obtained to permit determination of physical constants or electric moments. Several aldol type condensation reactions were tried with acetone and acetaldehyde. Proportions for the reactions were based on the preparation for benzalacetone submitted for Organic Syntheses by N. L. Drake and P. Allen, Jr.¹⁶ Various temperatures and times for the aldol type reactions were tried, but very little or none of the desired product was obtained. Other attempts were made using the method of Wohl and Maag,¹⁷ in which dry hydrogen chloride was passed through a mixture of acetone and paraldehyde. These attempts likewise were not fruitful.

Measurements and Calculations

Dielectric constants of solutions were measured at 25°C. by the heterodyne beat method as described by Otto and Wenzke¹⁸, using the carrier wave of a local radio station as a source of fixed radio frequency (Radio Station KSEL, frequency 950 KC, Lubbock, Texas). The circuit diagram for the variable frequency oscillator was taken from the oscillator section of a diagram for an apparatus by Chien¹⁹. The oscillator is of the negative transconductance type, which makes use of the particular electrode arrangement of a 6A8 type pentagrid converter tube which exhibits a negative transconductance between the signal grid, G4, and the anode grid, G2. This permits regenerative feed-back via condenser coupling between the two grids.

A dielectric cell (type 2TN 100A) of approximately 100 mmfd., with concentric nickel plates, manufactured by J. C. Balsbaugh, Cambridge, Massachusetts, was used. Glass inlet and outlet tubes were attached to the cell for convenience in filling and emptying the cell without removing it from the oil bath.

Equipment pictures and diagrams are contained at the end of this thesis.

Densities of solutions were obtained with a calibrated pycnometer with a volume of approximately thirty milliliters.

Molar refractions listed in Table III were obtained from the refractive indices and densities of the purified compounds, except that for methyl isopropenyl ketone the refraction information reported by Brant²⁰ was used.

Polarizations at infinite dilution were calculated by the method of Hedestrand²¹ as modified by LeFevre and Vine²² for calculating specific polarization. Solute concentrations were prepared in terms of weight fraction, rather than mol fraction, since it has been experimentally shown that the dielectric constant and density are generally linear functions of concentration expressed in this unit as well. Calculations of specific polarization based on weight fractions do not require any recognition of the molecular weight of the solvent, and thus are much simplified over calculations based on mol fractions.

The basic equation for the specific polarization of a solution may be taken to be:

$$(1) \quad p_{12} = p_1 w_1 + p_2 w_2 = \frac{\epsilon_{12}-1}{\epsilon_{12}+2} \times \frac{1}{D_{12}} = \frac{\epsilon_1-1}{\epsilon_1+2} \times \frac{w_1}{D_1} + p_2 w_2$$

p, specific polarization; w, solute weight fraction; ϵ , dielectric constant; D, density; 1, solvent; 2, solute; 12, solution.

From equation (1) there is readily obtained:

$$(2) \quad p_2 w_2 = \frac{\epsilon_{12}^{-1}}{\epsilon_{12} + 2} \times \frac{1}{D_{12}} - \frac{\epsilon_1^{-1}}{\epsilon_1 + 2} \times \frac{w_1}{D_1}$$

Differentiation of equation (2) with respect to weight fraction of solute, w_2 , and subsequent algebraic steps yield the following:

$$(3) \quad p_2 + w_2 \frac{\partial p_2}{\partial w_2} = \frac{3 \frac{\partial \epsilon_{12}}{\partial w_2}}{D_{12}(\epsilon_{12} + 2)^2} + \frac{\epsilon_1^{-1}}{\epsilon_1 + 2} \times \frac{1}{D_1} - \frac{\epsilon_{12}^{-1}}{\epsilon_{12} + 2} \times \frac{\partial D_{12} / \partial w_2}{D_{12}^2}$$

When $w_2 = 0$, then $D_{12} = D_1$, $\epsilon_{12} = \epsilon_1$, and $w_2 \frac{\partial p_2}{\partial w_2} = 0$, and there is obtained the following simpler expression:

$$(4) \quad p_{2\infty} = \frac{3 \frac{\partial \epsilon_{12}}{\partial w_2}}{D_1(\epsilon_1 + 2)^2} + \frac{\epsilon_1^{-1}}{\epsilon_1 + 2} \times \frac{1}{D_1} \left[1 - \frac{\partial D_{12} / \partial w_2}{D_1} \right]$$

It has been found empirically, in the absence of solute association and other abnormalities, that the ratios $\partial \epsilon_{12} / \partial w_2$ and $\partial D_{12} / \partial w_2$ are independent of concentration in dilute solution. The following simplifications are then justified:

$$\frac{\partial \epsilon_{12}}{\partial w_2} = \frac{\Delta \epsilon}{w_2} = \frac{\epsilon_{12} - \epsilon_1}{w_2}; \quad \frac{\partial D_{12}}{\partial w_2} = \frac{\Delta D}{w_2} = \frac{D_{12} - D_1}{w_2}$$

On this basis the polarization at infinite dilution, $p_{2\infty}$, should be calculable from the dielectric constants and densities of the solvent and one solution. However this

assumption of complete linearity is not reliable, and it is customary to investigate several solutions in the dilute region. The values of $\Delta\epsilon/w_2$ for the several solutions are plotted against w_2 as abscissa, and the graph extrapolated to $w_2 = 0$ to obtain a more reliable value of this ratio for purposes of calculating the polarization at infinite dilution.

In view of the foregoing, and further algebraic rearrangement, a convenient working formula for specific polarization at infinite dilution is:

$$(5) \quad p_{2\infty} = \frac{(\epsilon_1 - 1/\epsilon_1 + 2)(D_1 - \Delta D/w_2) + [3D_1/(\epsilon_1 + 2)^2] \cdot \Delta\epsilon/w_2}{D_1^2}$$

As indicated previously the ratios $\Delta\epsilon/w_2$ and $\Delta D/w_2$ are values obtained by extrapolation to $w_2 = 0$.

The molar polarization is readily obtained from the following equation:

$$(6) \quad P_{2\infty} = p_{2\infty} M \quad \text{where } M \text{ is solute mol. wt.}$$

Electric moments in Debye units were calculated from the usual equation:

$$(7) \quad \mu = 0.221(P_{2\infty} - 1.05 MR_D)^{\frac{1}{2}} \quad (\text{at } 25^\circ\text{C.})$$

MR_D is the molar refraction of solute for the sodium D line.

Accuracy of Results. The great precisions of the heterodyne beat method and the analytical balance used for weighings in solution preparations are such that these are not the significant factors in limiting the accuracy of electric moment determinations. Instead, accuracy limitation is mainly dependent upon such factors as oscillator stability, precision condenser calibration, technique in solution preparation, and carefulness of the worker. A condenser calibration chart furnished at extra cost by the condenser manufacturer was used. The condenser was also calibrated independently in connection with this work, and the results of both calibrations were consistent. Extrapolation of the dielectric slopes to infinite dilution were subject to some slight doubt, and to this extent the calculated moments are subject to some error. The equipment which was constructed for this work was tested by a trial determination of the electric moment of p-nitroaniline in benzene solution, and the value obtained for the moment agreed within ± 0.02 Debye units with a value of 6.31 D. previously determined by Curran and Estok¹⁰. The consistencies of the moments determined in benzene and dioxane solutions also indicate the general reliability of the results.

Experimental Results

Table II

Dielectric Constants and Densities
of Solutions at 25°C.

<u>Wt. %</u>	<u>ϵ</u>	<u>d</u>
Mesityl oxide (Benzene)		
0.0000	2.2730	0.87327
2.5051	2.4879	.87249
3.6799	2.5917	.87220
5.0624	2.7152	.87199
Mesityl oxide (Dioxane)		
0.0000	2.2154	1.02783
1.6215	2.3800	1.02428
2.3691	2.4588	1.02259
3.6482	2.5793	1.02003
4.8126	2.7131	-----
Methylmesityl oxide (Benzene)		
0.0000	2.2730	0.87327
1.0559	2.3558	.87320
1.7182	2.4101	.87314
2.8747	2.5032	.87306
5.6454	2.7304	-----
Methylmesityl oxide (Dioxane)		
0.0000	2.2154	1.02783
1.6100	2.3662	1.02461
2.2714	2.4300	1.02337
2.8710	2.4858	1.02217
4.6230	2.6544	-----

<u>Wt. %</u>	<u>ϵ</u>	<u>d</u>
Methyl isopropenyl ketone (Benzene)		
0.0000	2.2730	0.87339
1.6342	2.4298	.87280
3.3910	2.6016	.87225
5.0816	2.7724	.87173
Methyl isopropenyl ketone (Dioxane)		
0.0000	2.2077	1.02828
1.4108	2.3711	1.02524
2.9341	2.5485	1.02190
4.4451	2.7291	1.01864
3,4-Dimethyl-4-penten-2-one (Benzene)		
0.0000	2.2730	0.87327
2.421	2.4221	.87222
2.5044	2.4278	-----
3.482	-----	0.87177
3.9519	2.5176	-----
5.955	2.6423	0.87075
3,4-Dimethyl-4-penten-2-one (Dioxane)		
0.0000	2.2154	1.02783
1.9471	2.3568	1.02331
2.9750	2.4329	1.02088
5.1348	2.5979	1.01577
Methyl ethyl ketone (Benzene)		
0.0000	2.2730	0.87327
2.1063	2.5104	.87170
2.5797	2.5645	.87129
3.4337	2.6614	.87064
4.3626	2.7697	.86988
Methyl ethyl ketone (Dioxane)		
0.0000	2.2164	1.02790
3.1773	2.6467	1.01885
3.9756	2.7573	1.01673
4.5358	2.8326	1.01505
5.0766	2.9099	1.01349

<u>Wt. %</u>	<u>ε</u>	<u>d</u>
Methyl isopropyl ketone (Benzene)		
0.0000	2.2730	0.87339
2.6207	2.5199	.87124
4.3023	2.6826	.86991
6.0872	2.8577	.86849

Table III

Slope-Intercept Data, Polarizations, and Electric Moments (25°C.)

Solute	Solvent	$\frac{\Delta(\Delta\epsilon/w_2)}{\Delta w_2}$	$\frac{(\Delta\epsilon/w_2)_\infty}{\Delta w_2}$	$\frac{\Delta(\Delta d/w_2)}{\Delta w_2}$	$\frac{(\Delta d/w_2)_\infty}{\Delta w_2}$	$P_{2\infty}$	MR_D	μ
Mesityl oxide	Benzene	5.5	8.45	0.22	-0.036	191.0	(30.08)	2.79
	Dioxane	5.6	10.07	0.00	-0.220	195.8		2.83
Methylmesityl oxide	Benzene	3.4	7.91	0.021	-0.008	205.7		2.88
	Dioxane	3.5	9.32	0.10	-0.200	209.3	(34.62)	2.91
Isopropenyl methyl ketone	Benzene	6.9	9.48	0.065	-0.036	179.7		2.74
	Dioxane	5.9	11.47	0.00	-0.216	186.5	(25.05) ²⁰	2.80
3,4-dimethyl 4-penten-2-one	Benzene	1.0	6.14	0.032	-0.044	169.9		2.56
	Dioxane	6.4	7.12	-0.06	-0.232	169.7	(22.99)	2.56
Ethyl methyl ketone	Benzene	4.3	11.18	-0.08	-0.074	177.9		2.76
	Dioxane	3.8	13.44	-0.08	-0.280	181.6	(20.69)	2.82
Isopropyl methyl ketone	Benzene	5.4	9.28	0.034	-0.083	182.6	(25.29)	2.76

(Benzene, $\epsilon = 2.273$, $d = 0.873$; Dioxane, $\epsilon = 2.21$, $d = 1.028$)

DISCUSSION OF RESULTS

When values for electric moments are hereinafter indicated without reference to method of measurement or solvent, values determined in benzene solution are understood.

The moment of 2.79 for mesityl oxide is only slightly higher than the average moment of about 2.75 for saturated aliphatic methyl ketones, and considerably lower than that for methyl vinyl ketone, 2.98²³. A value of 2.84 has been previously reported for mesityl oxide by Bentley, et al.⁵, but treatment of their data by the method of this work yields 2.81.

The low moment for mesityl oxide is attributed to the predominance of the s-cis preferred configuration of the molecule. Fischer-Hirschfelder models indicate that steric hindrance and repulsion exist between methyl groups in the s-trans configuration of this molecule, in which form polar resonance structures such as

would greatly augment the primary carbonyl moment. μ_1 represents the main carbonyl moment, and μ_2 represents the

additional polarity due to resonance contribution. In an analogous case trans-crotonaldehyde, which does not have a hindering beta-methyl group, is able to exist predominantly in the s-trans configuration and yields a moment of 3.54 (in carbon tetrachloride solution) as compared to 2.90 for acrolein⁵. In the s-cis configuration for mesityl oxide, however, the polar resonance structures contribute only a very little to the total moment; i.e.,

Instances were given in Table I showing the influence of an alpha-methyl group in causing a reduction in moment. This effect is attributed to the moment, μ_3 , set up by alpha-methyl hyperconjugation in opposition to the primary moment, which is possible only if the molecule exists predominantly in the s-trans form as shown below.

When the beta-carbon is disubstituted, steric hindrance occurs in the s-trans form so that the s-cis configuration is favored. It is generally agreed, however, that in the

absence of any steric factors the s-trans form is a more stable form than the s-cis. However, when the s-cis form does predominate, the alpha-methyl hyperconjugation leads to an augmentation of the electric moment. This is well illustrated by a comparison of the moments of mesityl oxide and methylmesityl oxide, which compounds must be considered to exist predominantly in the s-cis form.

Mesityl oxide, 2.79

Methylmesityl oxide, 2.88

Due to the favored stability of the s-trans form this configuration may be expected to predominate for methyl vinyl ketone, and the high moment of 2.98 for this ketone illustrates how resonance in the s-trans form augments the electric moment. The following illustrate this effect.

Methyl vinyl ketone, 2.98

Methyl ethyl ketone, 2.76

The value of 2.74 for methyl isopropenyl ketone illustrates how the augmenting (conjugation) and opposing (hyperconjugation) effects cancel to yield a moment essentially

equal to that for methyl isopropyl ketone, 2.76. The influence of the additional alpha-methyl group reduces the electric moment from 2.98 (for methyl vinyl ketone) to the considerably lower value of 2.74.

Methyl vinyl ketone, 2.98

Methyl isopropenyl ketone, 2.74

Some doubt may exist as to the value of 2.74 for methyl isopropenyl ketone, however, because of the reported instability of this compound²⁰; however the index of refraction of this material did not change appreciably in two days, and a satisfactory boiling point was determined almost a month later.

The low moment of 2.56 for the non-conjugated case of 3,4-dimethyl-4-penten-2-one shows the influence of an isolated methylene group with hyperconjugation in opposition to the primary carbonyl moment, and confirms the sense of the moment of a group analogous to that in isobutylene.

The moments determined in dioxane solution lead to the same general configurational conclusions as those studied

in benzene solution. The dioxane data indicate only a small solvent effect tending to increase apparent moment by about 0.05 Debye units whether the ketone is unsaturated or not. This small increase in apparent moment may be due somewhat to the lower dielectric constant of the solvent dioxane compared to benzene, or perhaps partly to electrostatic interaction between dioxane and the carbonyl group as indicated below.

There is no definite evidence that dioxane stabilizes hyperconjugated structures through electrostatic interaction; however the compounds studied have been revealed to have structures such as would not be suitable for the observation of such an effect. An exception might be the case of the non-conjugated 3,4-dimethyl-4-penten-2-one, for which the identical moments obtained in benzene and dioxane might suggest solvent interaction with the hyperconjugated methyl group to counterbalance the small augmenting influence on the carbonyl moment. The data, however, are insufficient for any definite conclusion.

SUMMARY AND CONCLUSIONS

Electric moments were determined for the following methyl ketones in benzene and dioxane solutions:

Mesityl oxide
Methylmesityl oxide
Methyl isopropenyl ketone
3,4-Dimethyl-4-penten-2-one
Methyl ethyl ketone

A further moment was determined for methyl isopropyl ketone in benzene solution.

From the electric moments of these ketones, and a consideration of the literature concerning related compounds, the following observations and conclusions are made.

- 1) Alpha-methyl group hyperconjugation in conjunction with the s-trans configuration of an alpha-beta unsaturated aliphatic methyl ketone leads to a reduction in the electric moment; i.e., methyl vinyl ketone, 2.98 D. and methyl isopropenyl ketone, 2.74 D.
- 2) Alpha-methyl group hyperconjugation in conjunction with the s-cis configuration leads to an augmentation of the moment; i.e., mesityl oxide, 2.79 D. and methylmesityl oxide, 2.88 D.

- 3) Steric effects appear to favor the s-cis configuration when no hydrogen is present on the beta-carbon.
- 4) There was no definite evidence that the solvent dioxane interacted electrostatically with solute molecules to stabilize hyperconjugated methyl groups.
- 5) The slightly higher moments in dioxane solution compared to benzene solution may be due to the relatively lower dielectric constant of dioxane compared to benzene, or to electrostatic interaction between dioxane and the carbonyl group.

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THERMOREGULATOR RELAY OIL STIRRER MOTOR THERMOREGULATOR WATER STIRRER

PRECISION CONDENSER
DIELECTRIC CONSTANT APPARATUS

WATER BATH AND ASSOCIATED EQUIPMENT

WATER BATH AND ASSOCIATED EQUIPMENT

VARIABLE OSCILLATOR CIRCUIT DIAGRAM

CHASSIS

L1 APPROX. 30 TURNS OF #25 INSULATED WIRE ON 1.5" COIL FORM

C1 100-1100 μ F PRECISION CONDENSER

C2 DIELECTRIC CELL - APPROX. 96 μ F

C3 0.01 μ F - 600V PAPER

C4 0.005 μ F MICA

C5 8 μ F 450V ELECTROLYTIC

C6 300 μ F MICA

C7 .002 μ F

C8 0-50 μ F AIR TRIMMER

R1 500 Ω 1 WATT

R2, R6 50,000 Ω 1 WATT

K3 7,000 Ω 1/2 WATT

R4 15,000 Ω 1 WATT

R5 25,000 Ω 1 WATT

R7 0.5 MEGOHM 1/4 WATT