

line dihydrochloride is the loss of a proton from the "meta" nitrogen N⁴, according to Equation (2). It follows that the secondary dissociation results from the removal of a proton from N¹, the "para" nitrogen as shown in Equation (3).

TABLE III
COMPARATIVE SUBSTITUENT CONSTANTS

Group	σ_Q	σ_H	r	σ_A	$\sigma_Q - \sigma_H$	$\sigma_A - \sigma_H$
<i>p</i> -CH ₃ O	-0.42	-0.268	0.063	-0.67	-0.15	-0.40
<i>p</i> -CH ₃	-.13	-.170	.080	-.45	+.04	-.28
<i>m</i> -CH ₃	+.08	-.069	.045	-.07	+.15	.00
<i>m</i> -CH ₃ O	+.18	+.115	.102	+.42	-.06	+.30

In Table III the substituent constants calculated for the methyl and methoxy groups from data obtained in this investigation are tabulated under σ_Q . σ_H is the average value of the substituent constant according to Hammett, r denotes the median deviation of the value of σ_H , and σ_A is the substituent constant of substituted anilines¹⁶ only. From the relative magnitudes of the deviations in the last two columns it can be seen that the sigma values determined in this study approach, in general, Hammett's average values more closely than do those of the structurally simpler aniline system. An exception is evident in the small positive value of σ_Q found for the *m*-CH₃ group when compared with the small negative value of σ_H determined from thirty-two equilibrium and rate constants. Here the weak electron-releasing effect is reversed and the *m*-CH₃ groups seems to exhibit a weak attraction for electrons. Oddly enough the sigma value for *m*-toluidine shows excellent agreement with σ_H in both magnitude and sign, in contrast to the deviations observed when *p*-toluidine, *m*-anisidine, and *p*-anisidine are compared.

In view of the numerous experimental findings

(16) Hall and Sprinkle, *THIS JOURNAL*, **54**, 3469 (1932).

that support the weak electronegativity of the *m*-CH₃ group in monofunctional systems, any rational interpretation of the apparent electropositivity discovered in this work is subject to several considerations. In the first place, the stereochemical departure from simple side chains to bifunctional heterocyclic structures adumbrates an alteration of electron density within the molecules. Secondly, the supposition that "meta" and "para" positions exist between the substituent and each amino group, independent of a possible *proximity effect* arising from vicinal nitrogen atoms, implies an absence of ortho interaction. However, by comparing σ_Q with σ_H in Table III it is readily seen that the order of electronegativity (*p*-CH₃O > *p*-CH₃ > *m*-CH₃ > *m*-CH₃O) found by other workers is substantiated qualitatively by this research notwithstanding the presence of one or more superimposed or second-order effects.

Acknowledgment.—One of us (G. W.) wishes to express his appreciation to Mr. Albert Resnick for preparing most of the 1,2,3,4-tetrahydro-6-methylquinoxaline used in this work.

Summary

Solutions of the dihydrochlorides of 1,2,3,4-tetrahydroquinoxaline, 1,2,3,4-tetrahydro-6-methylquinoxaline and 1,2,3,4-tetrahydro-6-methoxyquinoxaline in the concentration range of 0.015–0.048 molar were titrated potentiometrically with standard base. Thermodynamic acidity constants were calculated for these compounds after ionic strengths and suitable corrections for activity coefficients had been determined.

The *sigma values* or *substituent constants* for the *m*-CH₃, *p*-CH₃, *m*-CH₃O and *p*-CH₃O groups calculated from *pK*'s show substantial agreement with those given by Hammett.

LEXINGTON, KENTUCKY RECEIVED JANUARY 16, 1950

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MARYLAND]

The Electric Moments of Some Keto and Hydroxy Derivatives of Cyclohexane

BY W. J. SVIRBELY AND JOHN J. LANDER¹

The electric moments² of the various dihydroxy derivatives of benzene were determined recently. It was deemed worthwhile to measure the electric moments of some analogous saturated cyclic compounds and also of some keto derivatives of cyclohexane, particularly those which on enolization would lead to structures which at least partially resembled those of the corresponding dihydroxy benzenes. Consequently, the electric

moments of *cis*-cyclohexanediol-1,2, *trans*-cyclohexanediol-1,2, *cis*-cyclohexanediol-1,4, *trans*-cyclohexanediol-1,4, cyclohexanedione-1,2 and α -hydroxycyclohexanone have been measured in benzene. An attempt is made to correlate the results with the possible structures of those compounds.

Materials and Experimental Procedure

Benzene.—The benzene was purified and the measurements of dielectric constant were made by means of the heterodyne beat apparatus and by methods previously described.³

cis and *trans*-Cyclohexanediol-1,2.—The crude mixture of isomers was prepared by hydrogenating catechol in ethanol over Raney nickel at about 195°. The crude

(1) (a) Part of a thesis submitted by John J. Lander to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1948. (b) Presented in part at the Atlantic City meeting of the American Chemical Society, September, 1949.

(2) Lander and Svirbely, *THIS JOURNAL*, **67**, 322 (1945).

mixture, after removal of the solvent under vacuum, melted at 72–75°. The *trans* diol was crystallized from this mixture in benzene by slow cooling and removal of successive amounts of the solid until the melting point began to drop sharply. This solid was recrystallized several times from benzene until the resulting *trans* diol had a constant m. p. of 103–104° (uncor.). Literature³ m. p. is 104°. The *cis* rich solution was treated by the method of Wilson and Read.⁴ The resulting *cis* diol had a constant m. p. of 98–99° (uncor.). Literature^{3,4} value is the same. Since the melting points of catechol and the diol isomers are close, mixed melting points were determined for all combinations. All mixtures gave large depressions.

cis and *trans* Cyclohexanediol-1,4.—The crude mixture of isomers was prepared by hydrogenating hydroquinone in ethanol over Raney nickel at about 176°. The m. p. of the mixture was 98–100°. The *trans* isomer was separated by slow crystallization from a 50–50 benzene–acetone mixture. Several recrystallizations gave a constant m. p. of 141–141.5° (uncor.). Literature⁵ value is 142°. The *cis* rich diol mixture was converted into diacetates. As much of the *trans* diacetate as possible was removed by crystallization from ether. Recrystallization of the *cis* rich diacetate mixture gave a material with a m. p. of 33°. An ester exchange reaction was then carried out using a 10 mole excess of methanol. After refluxing for three hours, the methyl acetate and the excess of methanol were slowly removed by fractionation. The resulting product was vacuum distilled (2–3 mm. pressure, 128°). The distillate was recrystallized four times to a constant m. p. of 111–112° (uncor.). Literature values for *cis*-cyclohexanediol-1,4 are 107°,⁵ 112°,^{6a} 112.4–112.8°.^{6b}

Cyclohexanedione-1,2.—The material⁷ was fractionated twice under vacuum. The center portion only was retained each time (19.3 mm., 81.5–83°). The fraction collected had a pale green tint. *Anal.* Calcd. for C₆H₈O₂: C, 64.27; H, 7.19. Found: C, 62.37; H, 7.20.

α -Hydroxycyclohexanone: Preparation 1.—The chlorination of 294 g. (3 moles) of freshly distilled cyclohexanone, diluted with 300 ml. of dry benzene, was accomplished by adding 228 ml. (3 moles) of sulfuryl chloride over a 2.5-hour period. Moisture was excluded and the temperature was kept at 16° by external cooling. After the solvent was removed under vacuum, the reaction mixture was fractionated (9 mm., 84°) and the chlorinated cyclohexanone was collected (yield, 67.6 g.). Hydrolysis was carried out by adding 400 g. of a 37.5% potassium carbonate solution and stirring vigorously with a Hershberg stirrer for 16 hours. The cream-colored, waxy product was leached with water, triturated with ether and filtered. Repeated crystallizations of the resulting solid from benzene yielded a white crystalline solid, m. p. 138–139° (uncor.) (yield, 3 g.). Literature values are 90° and 113°,^{8a} 132°,^{8b} and 130°.^{8c} *Anal.* Calcd. for C₆H₁₀O₂: C, 63.13; H, 8.83. Found: C, 63.18; H, 8.90. The m. p. of the above solid dropped to 112–114° after remaining in a closed bottle for one year. Reanalysis of the material gave C, 62.98; H, 8.75. The first run reported in Table I was made on the 112–114° material.

Preparation 2.—Freshly distilled cyclohexanone was chlorinated with chlorine gas in glacial acetic acid.⁹ The chlorinated compound was hydrolyzed as before. The white, waxy solid was distilled^{8c} (13–15 mm., 82–85°). A clear, colorless liquid was obtained and was used immediately for dielectric constant measurements (run no. 2).

(3) Rothstein, *Ann. Chim.*, **14**, 481 (1930).

(4) Wilson and Read, *J. Chem. Soc.*, **147**, 1270 (1935).

(5) Olberg, Pines and Ipatieff, *THIS JOURNAL*, **66**, 1096 (1944).

(6a) Coops, *et al.*, *Rec. trav. chim.*, **57**, 303 (1938).

(6b) Perrine and White, *THIS JOURNAL*, **69**, 1542 (1947).

(7) We are indebted to Dr. G. Frederick Smith of the University of Illinois for this compound.

(8) (a) Kotz and Gethe, *J. prakt. Chem.*, [2] **80**, 488 (1909); (b) Charlton, *et al.*, *J. Chem. Soc.*, 30 (1932); (c) Bergmann and Gierth, *Ann.*, **448**, 48 (1936).

(9) Bartlett and Rosenwald, *THIS JOURNAL*, **56**, 1990 (1934).

TABLE I
SUMMARY OF DATA IN BENZENE

Data in parentheses have been taken from corresponding mole fraction plots.

$N_2 \times 10^4$	d	ϵ	P_2
Run no. 1, <i>cis</i> -cyclohexanediol-1,2 at 44°, $\mu = 2.32$			
0.0000	0.85213	2.2297	$P_\infty = 137$
2.1952	(.85271)	2.2444	134
2.9991	(.85288)	2.2508	140
3.9149	(.85311)	2.2567	137
4.9424	.85345	2.2638	137
6.3790	(.85373)	2.2732	136
Run 2, $P_\infty = 139$ at 44°, $\mu = 2.34$			
<i>trans</i> -cyclohexanediol-1,2 at 44°, $\mu = 2.36$			
0.0000	0.85216	(2.2303)	$P_\infty = 141$
1.5909	(.85258)	2.2411	140
3.1074	(.85301)	2.2516	139
4.6154	(.85343)	2.2626	139
6.3257	0.85389	2.2735	136
7.3118	(.85417)	2.2806	137
Run no. 2, $P_\infty = 145$ at 44°, $\mu = 2.40$			
Run no. 3, $P_\infty = 146$ at 45.3°, $\mu = 2.41$			
Run no. 1, <i>trans</i> -cyclohexanediol-1,4 at 46.1°, $\mu = 1.77$			
0.0000	0.85018	(2.2287)	$P_\infty = 93$
.1706	(.85025)	2.2291	99
.3257	.85030	2.2297	94
.4770	(.85039)	2.2302	87
.6459	.85048	2.2312	93
Run no. 2, $P_\infty = 96$, $\mu = 1.82$			
<i>cis</i> -Cyclohexanediol-1,4 at 46.1°, $\mu = 2.50$			
0.0000	0.85024	(2.2279)	$P_\infty = 153$
.3585	(.85038)	2.2299	152
.4870	(.85044)	2.2309	150
.6635	.85050	2.2324	155
.7942	(.85055)	2.2336	155
1.1784	(.85070)	2.2368	155
Cyclohexanedione-1,2 at 46.1°			
0.0000	0.85014	2.2271	$P_\infty = 181$
5.7627	.85176	2.2835	179
7.5756	(.85244)	2.3034	181
8.2218	(.85263)	2.3115	184
11.2410	.85362	2.3421	182
α -Hydroxycyclohexanone at 46.1°			
Run no. 1, m. p. 114°, $\mu = 2.88$			
0.0000	0.85071	2.2282	$P_\infty = 192$
.4787	(.85086)	2.2330	185
.7182	.85088	2.2360	198
.9577	(.85101)	2.2380	186
1.4368	.85121	2.2443	200
Run no. 2 at 25.3° made on vacuum distilled liquid, $\mu = 2.92$			
0.0000	0.87210	(2.2553)	$P_\infty = 207$
2.2982	(.87285)	2.2855	207
5.4020	(.87345)	2.3151	208
8.3712	.87412	2.3522	208
10.4952	(.87465)	2.3761	205

TABLE II

Compound	$P_E + P_A$	$\mu \times 10^{18}$ exp.	Config. and calcd. moments	
<i>cis</i> -Cyclohexanediol-1,2	32.30	2.33 \pm 0.02	Bonded	2.6-3.3
			Free rotation	2.2
<i>trans</i> -Cyclohexanediol-1,2	32.30	2.39 \pm 0.03	2e, bonded	2.7-3.2
			2e, free rotation	2.2
			2p, restricted rotation	2.4
			2p, free rotation	2.1
<i>cis</i> -Cyclohexanediol-1,4	32.30	2.50 \pm 0.02	Free rotation	2.2
<i>trans</i> -Cyclohexanediol-1,4	32.30	1.80 \pm 0.03	2e, free rotation	2.2
			2e, restricted rotation	<2.2
			2p, restricted rotation	<2.1
Cyclohexanedione-1,2	29.12	2.80 \pm 0.02	Dione structure	3.7-4.2
Cyclohexanedione-1,2 (mono-enol)	29.17	2.80 \pm 0.02	Bonded, with resonance	2.8-3.0
			Free rotation	4.0
Cyclohexanedione-1,2 (di-enol)	31.32	2.78 \pm 0.02	Bonded, resonant hybrid	2.9-3.0
			Free rotation	2.2
α -Hydroxycyclohexanone	30.71	2.90 \pm 0.05	Ketone, e hydroxyl	2.0-2.5
			Ketone, p hydroxyl	2.0-2.5
			Ketone, free rotation	3.3
			Enol, bonded	2.8-3.0
			Enol, free rotation	2.2
Catechol ²		2.62		
Hydroquinone ²		1.4		
Cyclohexanedione-1,4 ²⁰		1.4	Ketone	0
			Mono-enol, free rotation of hydroxyl group	3.3
			Dienolic form, free rotation	2.2

Experimental Results

Some of the experimental results are given in Table I, which lists the mole fraction of the solute, N_2 ; the densities of the solutions, d ; the dielectric constants, ϵ ; the molar polarizations, P_2 ; and the extrapolated values of P_∞ obtained from the extrapolation of the polarization data given. For the check runs, the P_∞ values are given in Table I.

The molar refractions MR_D were calculated from the atomic refractions given in Landolt-Börnstein. The values of $P_E + P_A$ given in Table II were taken as 1.05 MR_D . The electric moments, calculated in the usual manner, are given in the third column of Table II.

Discussion

A number of investigations of cyclohexane and its derivatives have been carried out by Hassel¹⁰ using electron diffraction methods. Proof is advanced that substantially all of the compounds are in the more symmetrical chair form. Pitzer and his collaborators¹¹ have come to the same conclusion concerning cyclohexane and its dimethyl derivatives. Ottar,¹² making an electron diffraction investigation of the vapors of *cis* and *trans* cyclohexanediol-1,2, has come to the same conclusion concerning these two diols. Therefore, for the purpose of discussion, we shall assume the chair form for the derivatives of cyclohexane which were used in this investigation. We shall neglect any contributions of the boat form.

(10) O. Hassel, *Tids. Kjemi, Bergvesen*, **3**, 32 (1943).

(11) Beckett, Pitzer and Spitzer, *THIS JOURNAL*, **69**, 2488 (1947).

(12) B. Ottar, *Acta Chimica Scandinavica*, **1**, 521 (1947).

Several factors were considered in an attempt to reconcile the observed moments of the diols with values calculated on the basis of some definite molecular structures.

(a) **Tautomerism.**—As Hassel¹⁰ and Pitzer¹¹ have pointed out, if the carbon ring of the chair form of cyclohexane is viewed as horizontal, six of the hydrogens attached to the carbons will lie in an equatorial belt (e) and the remainder will be either above or below the ring (polar, p). When one or more of the hydrogens are replaced by different groups, tautomers are possible as the molecule changes from one chair form to another. As a result of this type of tautomerism, isomers in which both groups are either polar or equatorial are possible for the diols. Therefore, both structures must be considered in the calculations. Optical isomerism is also possible, but in this case one structure only has to be considered. Figure 1 and 2 illustrate the cases of *cis*-diol-1,2 and *trans*-diol-1,2, respectively. The solid lines pointing up and the dotted lines pointing down represent polar up and polar down groups, while the other lines represent equatorial groups. The number of structures which would have to be considered for all four diols are listed in the second column of Table III.

(b) **Hydrogen Bonding and Steric Hindrance.**—Examination of Fisher-Hirschfelder models indicates that internal hydrogen bonding is sometimes possible (see Table III). Models also indi-

TABLE III

Compound	Config.	Is internal H bonding possible?	Type of steric hindrance	$m_3m_2/d^3 \times 10^{14}$
<i>cis</i> -Diol-1,2	1e, 1p	Yes	Both	~ 13
<i>trans</i> -Diol-1,2	2e	Yes	Hydroxyl H's	~ 13
	2p	No	C ³ H	~ 9
<i>cis</i> -Diol-1,4	1e, 1p	No	C ³ H	~ 3
<i>trans</i> -Diol-1,4	2e	No	None	~ 1.8
	2p	No	C ³ H	~ 3

cate that two types of steric hindrance are encountered: (1) interference of hydroxyl hydrogens; (2) interference of polar hydroxyl hydrogens with polar hydrogens attached to carbons twice removed from the carbons bearing the hydroxyl hydrogens. The latter is indicated as C³H in Table III.

(c) **Interaction Energies.**—By use of 1.7 *D* (Debye units) as the group moment of COH and *d* as the distance between the oxygen atoms, interaction energies for the substituted groups were calculated.¹³ These values are listed in the last column of Table III. When possible, values of *d* were calculated by use of bond distances given by Pauling.¹⁴ Otherwise, they were estimated from models. Qualitative considerations have shown¹³ that if the interaction energy is of the order of magnitude of 4×10^{-14} ergs per molecule, free rotation will be greatly restricted and the measured moment different from the calculated moment based on free rotation. The moments designated as free rotation in the last column of Table II were obtained by use of an equation previously derived.¹⁵

In the cases of *cis* and *trans*-cyclohexanediol-1,2 it is apparent that the high values of the interaction energy and the existence of steric hindrance eliminate free rotation. Models indicate that hydrogen bonding could exist in both the 2e *trans*-diol-1,2 and the *cis*-diol-1,2 configurations. Now if: (1) it is assumed that hydrogen bonding exists; (2) the angles between the group moments are approximated from a model; (3) the commonly accepted values¹⁶ for the group moments are used; then the electric moments can be shown to be in the ranges of 2.6–3.3 *D* and 2.7–3.2 *D* (depending on angle range estimated) for the *cis*-diol-1,2 and for the 2e *trans*-diol-1,2, respectively. Restricted rotation for the 2p *trans*-diol-1,2 gives a calculated value of 2.4 *D*. A choice between the 2p and 2e *trans*-diol-1,2 configurations is thus impossible on the basis of calculated moments alone. If Pitzer's¹¹ statement, that tautomers with polar substituents have higher energies than those with equatorial

(13) Meyer, *Z. physik. Chem.*, **83**, 27 (1930).

(14) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1940, 2nd ed., p. 167.

(15) Swirbely and Lander, *THIS JOURNAL*, **70**, 4121 (1948), equation 1.

(16) LeFèvre, "Dipole Moments," Methuen and Co., Ltd., London, England, 1938, p. 59.

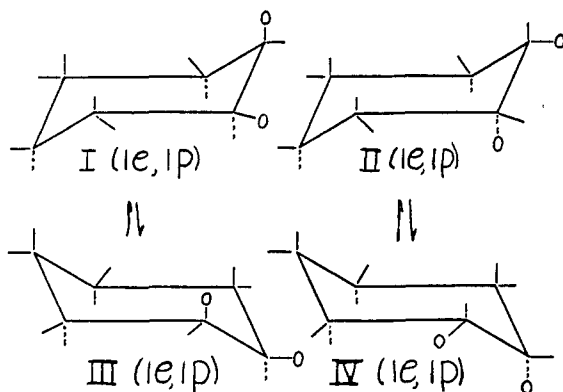


Fig. 1.—*cis*-Cyclohexanediol-1,2: I and II, III and IV are identical; I and III, II and IV are optical isomers.

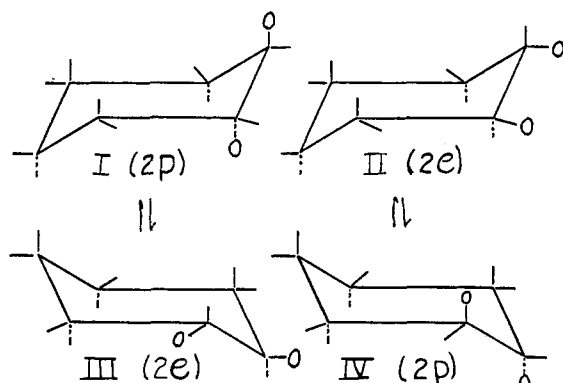


Fig. 2.—*trans*-Cyclohexanediol-1,2: tautomer of I is mirror image of II; tautomer of II is mirror image of I.

substituents, is applicable, then the 2e isomer should be favored over the 2p isomer. The close agreement in the measured moments of the *cis*-diol-1,2 and the *trans*-diol-1,2, and the close similarity in structures (assuming hydrogen bonding) of the *cis*-diol-1,2 and the 2e *trans*-diol-1,2 lead us to favor the 2e isomer.

For *cis*-cyclohexanediol-1,4, one configuration only is possible. The equatorial hydroxyl is free to rotate but the polar hydroxyl encounters hindrance. The high interaction energy and steric hindrance eliminate free rotation.

For *trans*-cyclohexanediol-1,4, reference to Tables II and III indicates that no choice is possible between the 2e and 2p configurations. Free rotation cannot exist. If Pitzer's rule concerning polar configurations is applicable, the equatorial structure should be favored.

Although the purity of cyclohexanedione-1,2 is in question, the effect of the impurities on the moment should be small. If one estimates the angles from a model (allowing for a 10° error) and uses the usual group moments,¹⁶ then the calculated moment for the α -diketone structure is between 3.7–4.2 *D*. The experimental value is 2.8 *D*. Due to the conjugated system, resonance is possible (Structures I and II, Fig. 3).

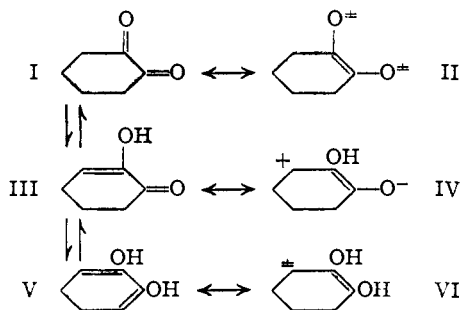


Fig. 3.

Such resonance should change the moment very little. The diketone, is, however, largely enolic.¹⁷ If it is assumed that we are dealing with a non-associated, single enolic tautomer, whose hydroxyl hydrogen is bridged to the carbonyl oxygen within the molecule, then the calculated moment is $2.02D$. However, in the singly enolized form, resonance could lead to a structure which would affect the electric moment markedly. For example, the moments of α,β , unsaturated aldehydes and ketones are considerably larger than those of the corresponding saturated compounds. The difference can be considered to be due to the possibility of resonance of the original unsaturated structure with one involving a polar structure.^{18,19} The above explanation is supported in cyclic compounds by the moments of 3,5-dimethylcyclohexenone and pulegone.¹⁹ Structures III and IV, Fig. 3, illustrate the resonant hybrid structure for the single enolic form of cyclohexanone-1,2. The moment of the singly enolized, resonant hybrid structure is recalculated

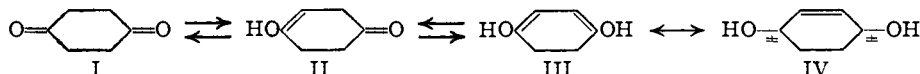


Fig. 4.

to be between $2.8-3.0D$, if the vector representing the ionic contribution is considered to be in full support of the ketone vector. The recalculated value is in very good agreement with experiment. However, tautomerism is possible between the single enolic structure and the dienolic structure (III and V, Fig. 3). Assuming a rigid molecule for the dienolic form, the moment is calculated to be about $2.9D$. Due to the conjugated system, the dienolic form can exist as a resonance hybrid (V and VI, Fig. 3). Although this would have little effect on the calculated moment of the dienolic structure, it would help to stabilize it. Thus, the calculated moment for the resonant hybrid of the dienolic structure is in very good

(17) Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 211.

(18) Hurdis and Smyth, *This Journal*, **65**, 89 (1943).

(19) (a) See ref. 17, page 134 for discussion. (b) "Dipole Moments," Transactions of the Faraday Society, September, 1934, Gurney and Jackson, London, England, gives values of 3.79 and 3.95 for 3,5-dimethylcyclohexenone and a value of 2.95 for pulegone. The difference between the two compounds is thus $0.9 \approx 0.1D$.

agreement with the experimental value. A choice between the single enolic resonant hybrid and the dienolic resonant hybrid cannot be made, therefore, on the basis of electric moments alone. However, the similarity in structure between catechol and the dienolic structure (V, Fig. 3), and the rather close agreement in their measured moments (Table II) lead us to favor the dienolic resonant hybrid as being the predominating form. Free rotation can be eliminated on the same grounds as used for the 1,2 diols.

In connection with the cyclic diones, the moment of cyclohexanedione-1,4 has been shown²⁰ to be $1.4D$. Since the moment should be zero if the chair form of the diketone structure exists, the above value was explained²⁰ on the basis of a mixture of chair and boat forms. If the conclusions of other workers^{10,11,12} concerning the prevalence of the chair form over the boat form for cyclohexane and its derivatives are applicable to cyclohexanedione-1,4, then this explanation is questionable. Referring to Fig. 4, one observes the possible structures as a result of keto-enol tautomerism and resonance. Structure I, in the chair form, should have zero moment. The single enolic tautomer (II) has a free rotation value of $3.3D$. The dienolic structure (III) has a free rotation value of $2.2D$. However, both of these values are high. Due to the conjugated system, the dienolic form can exist as a resonance hybrid (III and IV, Fig. 4), which will help to stabilize the structure. The agreement in the measured moments of cyclohexanedione-1,4 and hydroquinone (Table II) and the similarity in their ring structures lead us to favor the dienolic resonant hybrid as being the predominating form.

In the case of α -hydroxycyclohexanone, if the structure is written as the name suggests, two tautomeric forms must be considered: (1) one having a polar hydroxyl group; (2) the other having an equatorial hydroxyl group. By use of the same procedures as before, moments in the range of $2-2.5D$ are calculated for both tautomers. Reference to Table II will show that neither of these values is consistent with the experimental value of $2.9D$. Free rotation in either case can be eliminated as a result of both steric hindrance and interaction energy. Infrared spectra²¹ of the solid form obtained in preparation No. 2 showed that the solid had a very weak carbonyl absorption peak. This may be interpreted as being due to either association or to enolization. Assuming,

(20) LeFèvre and LeFèvre, *J. Chem. Soc.*, 1696 (1935).

(21) We wish to acknowledge our indebtedness to Messrs. John French and L. W. Daasch and also to Dr. D. C. Smith, all of the Naval Research Laboratory, for their cooperation in obtaining and their assistance in interpreting the infrared absorption data on the compounds of this paper.

however, an enol structure as the basic form of the compound in dilute benzene solution, the calculated moment of α -hydroxycyclohexanone is found to be in the range of 2.8–3.0D. This value is in good agreement with the experiment. Free rotation of the enolic form is eliminated on the basis of the same reasoning as used for the 1,2 diols. Infrared spectra²¹ of the vacuum distilled liquid used in run no. 2 showed the presence of appreciable amounts of the carbonyl group and hence the liquid must be quite rich in the ketonic form. In benzene solution, however, the vacuum distilled liquid gave essentially the same experimental moment as the solid form used for run no. 1. Thus it may be concluded that α -hydroxycyclohexanone exists in benzene solution as a

mixture of isomers with the enolic form predominating.

Summary

1. The electric moments of *cis*-cyclohexanediol-1,2, *trans*-cyclohexanediol-1,2, *cis*-cyclohexanediol-1,4, *trans*-cyclohexanediol-1,4, cyclohexanedione-1,2 and α -hydroxycyclohexanone have been determined in benzene and are equal to 2.33, 2.39, 2.50, 1.80, 2.80, and 2.90D, respectively.

2. Limited conclusions as to the configurations of these compounds in benzene solution have been drawn on the basis of general theory and the experimental results.

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RECEIVED DECEMBER 15, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE ILLINOIS INSTITUTE OF TECHNOLOGY]

The Oxidation of Several Metals in Activated Oxygen at High Temperatures^{1,2}

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Introduction.—Heretofore kinetic studies on the oxidation of metal surfaces have been restricted to the use of free oxygen, or some oxidizing compound such as water vapor, carbon dioxide, oxides of nitrogen or ozone. Since it is well known that a properly regulated electric discharge can produce large quantities of oxygen atoms, it seemed worth while to ascertain experimentally the influence of such activated oxygen on the rate of oxidation of copper and other metals. The present paper reports a series of such measurements in the pressure range 0.5 to 2.0 mm. and at temperatures ranging from 500 to 690°.

Experimental

A continuous stream of activated oxygen^{4–10} was produced in the apparatus shown in Fig. 1. The oxygen pressure was maintained within ± 0.05 mm. in the range of pressures of 0.5–4.0 mm.; the linear flow rate of oxygen was 40–70 cm. per second, depending on the pressure of oxygen in the system. The electrical discharge through the activation tube was obtained by means of a 15 kv. transformer, and a current strength up to 68 ma. was employed.

The concentration of oxygen atoms^{11,12} was measured

(1) This research was generously supported by the U. S. Navy Office of Naval Research.

(2) From a thesis submitted to the Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Standard Oil Company (Indiana), Chicago, Illinois.

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(11) Gas withdrawn from the experimental space through a narrow glass tube (to effect recombination of the oxygen atoms) imparted very slight color to a potassium iodide-starch-glycerol paper. Ozone introduced into the system caused immediate coloration. Thus the concentration of ozone in the activated oxygen was negli-

gible. The absence of ozone in activated oxygen has been observed previously^{4,6} and explained by the low probability of the triple collisions necessary for the formation of ozone. The rate of decay of the "activity" of the activated oxygen is less than exponential with increase of distance downstream from the discharge. By extrapolation, one may estimate that 80% of the oxygen molecules are dissociated to atoms in the discharge.

(12) Measurements of the conductivity of the gas were made using a galvanometer in series with a 135 v. battery and two copper plates placed parallel 0.4 cm. apart in the experimental space. Within the limits of measurement (10^{-7} amp.) no current was observed so that the concentration of gaseous ions was at most negligible.

(13) Selected Values of Thermodynamic Constants, Natl. Bureau of Standards, Washington, D. C., 1947.