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Secondary α -Deuterium Isotope Effect. The Mechanism of the *cis-trans* Catalyzed Isomerization of Maleic Acid¹

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The secondary α -deuterium isotope effect in the potassium thiocyanate-catalyzed isomerization of maleic acid-2,3-*d*₂ has been measured over the temperature range 15 to 80°. From these data the net change in the carbon-hydrogen vibrational frequencies in going from the ground state to the transition state has been evaluated, and it appears as if the transition state lies a little more than half way along the path between a trigonal and tetrahedral carbon atom. The infrared spectrum of maleic anhydride-*d*₂ has been measured and compared with that for maleic anhydride.

Introduction

Streitwieser, *et al.*,² have observed that cyclopentyl tosylate-1-*d* is solvolyzed, in sodium acetate-acetic acid (S_N1 conditions) at 60°, at a slower rate than the protium analog ($k_H/k_D = 1.15$). They attribute this secondary α -deuterium isotope effect mainly to the large change in one of the carbon-hydrogen bending frequencies. As they have pointed out, a tertiary C-H exhibits a stretching frequency of 2890 cm.⁻¹ and a doubly degenerate bending frequency of 1340 cm.⁻¹. An aldehyde, which is chosen as a model for the cyclopentyl carbonium ion, possessing sp²-hybridization, exhibits a carbon-hydrogen stretching frequency of 2800 cm.⁻¹, an in-plane bending frequency of 1350 cm.⁻¹ and an out-of-plane bending frequency of 800 cm.⁻¹. The major change, therefore, in going from the ground state to transition state is the decrease in the out-of-plane C-H deformation frequency. The magnitude of the isotope effect for the complete change from tetrahedral to trigonal coordination was calculated by using an approximate form of the Bigeleisen³ equation.

$$\frac{k_H}{k_D} = \frac{K_H}{K_D} (\nu_{H,L} \mp / \nu_{D,L} \mp) \frac{s_H/s_D}{s_H \mp / s_D \mp} \frac{\prod_i \frac{u_{D_i}}{u_{H_i}} e^{(u_{H_i} - u_{D_i})/2} \frac{(1 - e^{-u_{H_i}})}{(1 - e^{-u_{D_i}})}}{\prod_i \frac{u_{D_i} \mp}{u_{H_i} \mp} e^{(u_{H_i} \mp - u_{D_i} \mp)/2} \frac{(1 - e^{-u_{H_i} \mp})}{(1 - e^{-u_{D_i} \mp})}} \quad (1)$$

Here K is the transmission coefficient, s the symmetry number, $\nu_{H,L} \mp / \nu_{D,L} \mp$ the ratio of frequencies along the reaction coordinate and u_i is equal to $hc\omega_i/kT$. By substituting 1340 and 800 cm.⁻¹ for ω_H and $\omega_H \mp$, respectively, in the zero point energy term and assuming all other ratios to the negligible k_H/k_D was calculated to be a maximum value of 1.44.

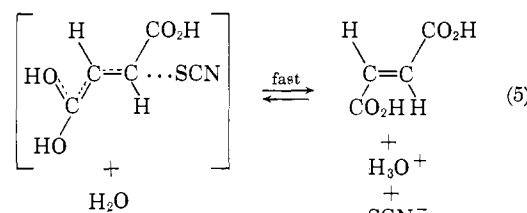
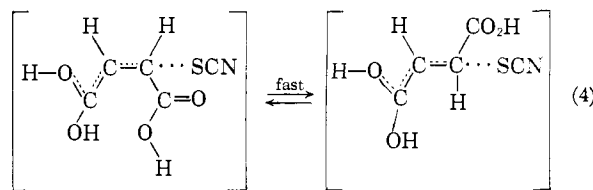
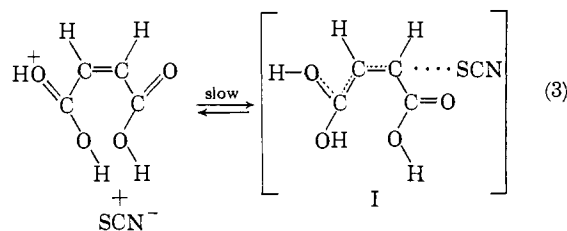
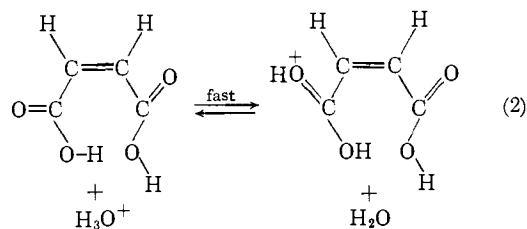
In order to test this interpretation of the secondary α -deuterium isotope effect, the *cis-trans* isomerization of maleic acid to fumaric acid, catalyzed by aqueous potassium thiocyanate, was measured. Nozaki and Ogg⁴ postulated the mechanism of catalytic isomerization to be

(1) (a) Research performed under the auspices of the U. S. Atomic Energy Commission. (b) A preliminary report appeared in *Chem. and Ind. (London)*, 1313 (1959).

(2) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958).

(3) J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949); *J. Phys. Chem.*, **56**, 823 (1952).

(4) K. Nozaki and R. Ogg, *J. Am. Chem. Soc.*, **63**, 2583 (1941).



If the ethylenic hydrogens are replaced by deuterium, an inverse secondary α -deuterium isotope effect is expected since in eq. 3, reaction from left to right, the ethylenic-carbon hybridized orbitals are being converted from sp² to sp³.

An examination of the temperature dependence of the isotope effect would yield the total net change in the carbon-hydrogen frequencies in going from the ground state (maleic acid) to the transition state (I). In addition, the ratio of the reduced masses along the reaction coordinate can be extracted from the temperature independent factor of eq. 1.

Experimental

Maleic Acid-2,3-*d*₂ Method I.—Eastman white label acetylenedicarboxylic acid (monopotassium salt) was titrated to

pH 6.5 with carbonate free sodium hydroxide. The solution was lyophilized and the salt was dried *in vacuo* over P_2O_5 . The salt was dissolved in D_2O and acidified with 19 $N D_2SO_4$. The carboxylic acid was extracted with ether and dried over Na_2SO_4 . The acid was obtained by evaporation of the ether.

Fifteen per cent. palladium on charcoal (1.36 g.) was suspended in 25 ml. of dry ether contained in a hydrogenation flask. The system was flushed with nitrogen several times and lastly with deuterium and the catalyst was allowed to adsorb deuterium. Then 3.85 g. of acetylenedicarboxylic acid- d_2 and another 25 ml. of dry ether were added. The required amount of deuterium was taken up in about 3 hr. whereupon the reaction was stopped. The catalyst was removed by filtration and the product was obtained by evaporation of the solvent.

The solid product was mixed with P_2O_5 and placed in a vacuum sublimator which was maintained at 80° and 0.3 mm. Maleic anhydride- d_2 condensed on the cold finger maintained at 0° . Another 3.30 g. of the acetylenedicarboxylic acid- d_2 was reduced and the product dehydrated in the same manner. The two samples of anhydride were combined and sublimed after which it was fractionated through a three-inch Vigreux column and then recrystallized from ether; m.p. $53.4\text{--}54.2^\circ$ (uncorr.).

Diluted Maleic Acid- d_2 .—The above anhydride, 0.4046 g., was mixed with 16.4261 g. of purified natural maleic anhydride. The anhydride was dissolved in water and allowed to remain at room temperature for 45 minutes before freezing and lyophilization, m.p. $139.7\text{--}140.0^\circ$ (corr.), lit. $138\text{--}139^\circ$.⁵ In this way at least 99.99% hydrolyzed⁶ and less than 0.015% isomerized to fumaric acid.⁷

Maleic Acid- d_2 Method II.—Five per cent. palladium on charcoal (1.18 g.) (Baker and Co. catalysts) in 10 ml. of fresh ethyl acetate was first equilibrated with deuterium gas. Then 3.50 g. of acetylenedicarboxylic acid dimethyl ester⁸ was added. The required amount of deuterium was taken up in 60 minutes. The solvent was evaporated off after filtering the mixture. The mixture of *cis* and *trans* isomers was distilled and the distillate suspended in about 50 ml. of water containing 1 ml. of 1.5 M nitric acid. The mixture was refluxed for 6 hr. after which the solution was lyophilized. The solid material was mixed with an equal quantity of P_2O_5 and placed in a vacuum sublimator. The sublimate, impure maleic anhydride, was then chromatographed as a 30% solution in ethyl acetate on a LAC-446 column in an Aerograph Vapor Phase Chromatog at 178° with a helium flow of 20 cc./min. The ethyl acetate appeared in less than one minute while maleic anhydride appeared after 10–11 minutes. The anhydride was collected in a trap cooled by liquid N_2 . The anhydride was once more sublimed at 50° and 0.1 mm.; m.p. $51.8\text{--}53.5^\circ$ (uncorr.). This method gave anhydride with a higher deuterium content than that produced by method I and was used for the infrared determinations. The acid was prepared from the anhydride in the same manner as described in method I.

Kinetic Runs.—Merck, reagent grade, potassium thiocyanate was dried and a 0.090 M solution was prepared. The appropriate amounts of maleic acid and stock KSCN solution were placed in a heavy walled test tube, sealed off and placed in a thermostated bath until approximately 10% of the starting material had isomerized. The tube was opened and the solution lyophilized. The calculated amount of water necessary to dissolve all the maleic acid was added. The residue was recrystallized twice from H_2O and dried over P_2O_5 at 80° *in vacuo*.

Deuterium Analysis.—Samples were burned in a combustion tube as described by Christman, *et al.*,⁹ and modified

(5) C. D. Hurd, A. S. Roe and J. W. Williams, *J. Org. Chem.*, **2**, 314 (1938).

(6) A. C. D. Rivett and N. V. Sidgwick, *J. Chem. Soc.*, **97**, 1677 (1910).

(7) (a) It is assumed that the rate constant for the autocatalytic isomerization of maleic acid is the same as that for the hydrochloric acid-catalyzed isomerization of maleic acid^{7b} since the nucleophilicity of Cl^- and acetate ion (a carboxylic acid anion) are about equal.^{7c} (b) K. Nozaki and R. Ogg, Jr., ref. 4. (c) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 140.

(8) Kindly donated by Dr. G. Juppe.

(9) D. R. Christman, N. E. Day, P. R. Hansell and R. C. Anderson,

so that the amount of non-heated glass was at a minimum. A Dry Ice-cooled U-tube, fitted with stopcocks, and 12/30 and 7/25 standard taper joints, fit directly on the end of the combustion tube. The water, after degassing, was reduced to hydrogen over hot uranium.¹⁰ The combustion line, U-tube and reducing apparatus were conditioned by running and discarding the first sample. In addition, samples were run in duplicate and sometimes triplicate. The hydrogen gas was analyzed for deuterium content with the aid of a Consolidated-Nier Isotope Ratio Mass Spectrometer used as a single collecting instrument. The observed ratios were compared to those observed for standard samples analyzed on the same day.

Infrared spectra were obtained by using a Perkin-Elmer Model 221 spectrometer with a sodium chloride prism for the region $4000\text{--}650\text{ cm.}^{-1}$ and a potassium bromide prism for the region $850\text{--}400\text{ cm.}^{-1}$. Samples were prepared as KBr pellets. The concentrations used were (see Fig. 1): 1A and 1C, 1.28 mg. of maleic anhydride in 361 mg. of KBr; 1B and 1D, 1.13 mg. of maleic anhydride- d_2 in 329 mg. of KBr.

Results and Discussion

Before measuring the secondary isotope effect it is necessary to consider the possibility of ethylenic-hydrogen exchange. Horrex¹¹ allowed maleic acid to isomerize in a solution of DCl and failed to find any deuterium in the product, fumaric acid. The absence of exchange was rechecked in this research by comparing the atom per cent. deuterium in the starting material with that in the fumaric acid after 93.8% of the maleic acid had isomerized in 0.090 M potassium thiocyanate at 80° . The results are shown in Table I. The observed atom per cent. D in fumaric acid is somewhat higher than in the starting material; this is to be expected.¹²

TABLE I

ATOM %D BEFORE AND AFTER ISOMERIZATION AT 80°	
No.	Atom %D
Maleic acid-2,3- d_2	28 0.890, 0.889, 0.906, 0.916
	29 .900, .887, .909, .909
	30 .888, .881, .890, .879
	Av. = 0.895 \pm 0.010
Fumaric acid-2,3- d_2	12 0.942, 0.930
	13 .914, .902, 0.910
	14 .946, .949
	15 .947, .939
	Av. = 0.931 \pm 0.015

The atom per cent. deuterium in the product at different temperatures of reaction is shown in Table II. It is necessary to correct the observed isotope effect in two ways: (1) for the fraction of reaction that the non-tracer molecules undergo¹³ and (2) for the reaction of maleic acid molecules containing deuterium and protium with rate constants k_H and k_D , respectively. The latter correction requires further comment.

Anal. Chem., **27**, 1935 (1955); D. R. Christman and C. Paul, *ibid.*, **32**, 131 (1960).

(10) J. Bigeleisen, M. L. Perlman and H. C. Prosser, *ibid.*, **24**, 1356 (1952).

(11) C. Horrex, *Trans. Faraday Soc.*, **33**, 570 (1937).

(12) Taking 0.895 as the atom % D in the starting material, the expected¹³ atom % D in the product after 93.8% reaction is 0.907.

(13) J. Bigeleisen, *Science*, **110**, 14 (1949).

From the quantities of natural and deuterated maleic anhydride used (see Experimental) to make up the maleic acid-2,3- d_2 mixture and from the measured atom percentage of deuterium in the mixture, the atom fraction of deuterium in the original deuterated maleic anhydride is calculated to be 0.742₁. Then, assuming statistical incorporation, maleic acid molecules derived from this deuterated maleic anhydride will be composed of 55.0₇ % 2,3- d_2 , 39.2₈ % 2- d_1 and 6.65 % 2,3- d_0 . The over-all mixture will then contain 1.30₄ % 2,3- d_2 , 0.907 % 2- d_1 and 97.78₉ % 2,3- d_0 maleic acid molecules.

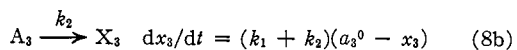
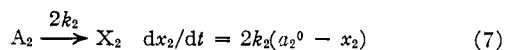
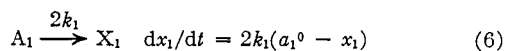
TABLE II

ATOM %D BEFORE AND AFTER ISOMERIZATION AT 15-80°

No.	Temp., °C.	f^a	Atom %D
22	15.1	0.10	1.010, 1.002
23	15.1	0.10	1.029, 1.014, 1.013, 1.000 Av. = 1.011 ± 0.007
24	25.0	0.11	0.989, 0.983
25	25.0	0.11	1.013, 1.025, 0.991, 0.987 Av. = 0.998 ± 0.014
18	40.0	0.10	1.008, 0.993, 0.971, 0.968
19	40.0	0.10	0.986, 0.999 Av. = 0.988 ± 0.013
20	60.0	0.10	0.991, 0.996
21	60.0	0.10	1.007, 1.006 Av. = 1.000 ± 0.007
26	80.1	0.11	0.976, 0.975
27	80.1	0.11	0.966, 0.960 Av. = 0.969 ± 0.006

^a f is the fraction of reaction undergone by the non-tracer molecules.

A substantial number of the deuterated molecules are singly deuterated. If, in these molecules, deuterium is at the 2 position and the thiocyanate ion attacks at the 3 position, the rate of isomerization is expected to be the same as that for those molecules which do not contain deuterium. The net effect, therefore, is to carry deuterium into the product with a rate identical with that for the protium compound (*i.e.*, no isotope effect). This can be corrected for in the following way. Let A_1 , A_2 and A_3 represent maleic acid-2,3- d_0 , -2,3- d_2 and -2- d_1 , respectively and X_1 , X_2 and X_3 their corresponding products. Then



where the lower case letters refer to concentrations. Integration yields

$$x_1 = a_1^0 (1 - e^{-2k_1 t}) \quad (9)$$

$$x_2 = a_2^0 (1 - e^{-2k_2 t}) \quad (10)$$

$$x_3 = a_3^0 (1 - e^{-(k_1 + k_2)t}) \quad (11)$$

where the zero superscripts refer to initial concentrations.

Define atom fraction of deuterium in the product mixture as f_D . Then

$$f_D = \frac{2x_2 + x_3}{4(x_1 + x_2 + x_3)} \quad (12)$$

Equation 13

$$f_D = \frac{2a_2^0(1 - e^{-2k_2 t}) + a_3^0(1 - e^{-(k_1 + k_2)t})}{4[a_1^0(1 - e^{-2k_1 t}) + a_2^0(1 - e^{-2k_2 t}) + a_3^0(1 - e^{-(k_1 + k_2)t})]} \quad (13)$$

is obtained from eq. 9, 10, 11 and 12. By expansion of the exponential terms and taking only the

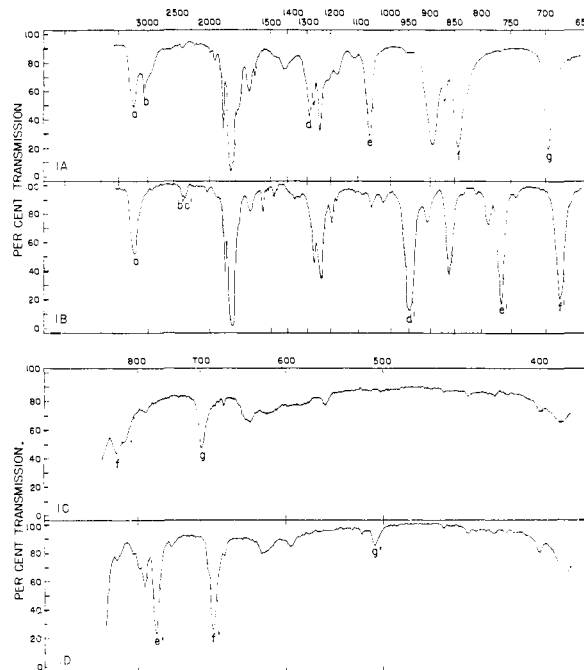


Fig. 1.—1A and 1C, maleic anhydride; 1B and 1D, maleic anhydride- d_2 . Carbon-hydrogen bands: b and b', symmetric stretch; c', asymmetric stretch; d and d', asymmetric in-plane bend; e and e', symmetric in-plane bend; f and f', asymmetric out-of-plane bend; g and g', symmetric out-of-plane bend. Band a is the oxygen-hydrogen stretching frequency due to moisture in the pellet.

first two terms (this approximation will be corrected for below), we find that

$$f_D = \frac{4a_2^0 k_2 + a_3^0(k_1 + k_2)}{4[2a_1^0 k_1 + 2a_2^0 k_2 + a_3^0(k_1 + k_2)]} \quad (14)$$

By solving for k_1/k_2 , eq. 15 is obtained.

$$k_1/k_2 = \frac{a_2^0 + a_3^0/4 - f_D(2a_2^0 + a_3^0)}{(2a_1^0 + a_3^0)f_D - a_3^0/4} \quad (15)$$

Correction 1 above refers to the well known correction of the observed isotope effect to zero per cent. reaction. Equation 16¹³ can be applied.

$$\frac{N_X}{N_{X_0}} = \frac{1 - (1 - f)^{k_2/k_1}}{f} \quad (16)$$

Here N_X is the atom per cent. deuterium in the product after non-tracer molecules have undergone fraction of reaction, f . N_{X_0} is the atom per cent. deuterium in the starting material.

Equations 15 and 16 were applied to the observed isotope effects and the corrected values are shown in Table III. The ratio of rate constants, k_H/k_D , in

TABLE III

SECONDARY α -DEUTERIUM ISOTOPE EFFECT BETWEEN 15 AND 80°

Temp., °C.	$(k_H/k_D)_{\text{obsd.}}$	k_H/k_D^a	k_H/k_D^b
15.1	0.885	0.850	0.842
25.0	.897	.863	.854
40.0	.906	.873	.866
60.0	.895	.861	.853
80.0	.924	.893	.886

^a Corrected by use of eq. 15. ^b Corrected by use of eq. 15 and 16.

Table III refers to rate constants for maleic acid-2,3- d_0 and -2,3- d_2 , respectively. This can be calculated by considering eq. 1 and by having a knowledge of the vibrational frequencies of the ground and transition states.

Temperature Dependence.—In calculating isotope effects by the use of eq. 1, the transmission coefficient ratio is assumed to be unity.¹⁵ In the case of the natural and doubly deuterated compounds, the symmetry number term reduces to unity. For frequencies greater than 3000 cm.^{-1} and for temperatures around 300°K., the ratio of the $(1 - e^{-u})$ terms approaches unity. In this instance, however, there are frequencies at about 700 and 850 cm.^{-1} and therefore these terms cannot be neglected. In the temperature range 15 to 80°, the product of the ratios changes less than 1% and therefore can be considered a constant equal to C . Finally, if the ratio $\omega_{D_i}/\omega_{H_i}$ is assumed to be equal to $\omega_{D_i}^\ddagger/\omega_{H_i}^\ddagger$ and represented by r_i , eq. 1 can be rewritten as

$$\frac{k_H}{k_D} = C \left(\frac{\nu_{H,L}^\ddagger}{\nu_{D,L}^\ddagger} \right) \prod_i e^{(hc/2kT)(1-r_i)(\omega_{H_i} - \omega_{D_i}^\ddagger)} \quad (17)$$

or

$$\log \frac{k_H}{k_D} = \log C \left(\frac{\nu_{H,L}^\ddagger}{\nu_{D,L}^\ddagger} \right) + \frac{1}{2.303} \sum_i \frac{hc}{2kT} (1 - r_i)(\omega_{H_i} - \omega_{D_i}^\ddagger) \quad (18)$$

If $\log k_H/k_D$ is treated as a linear function of $1/T$ by the method of least squares, the intercept and slope are 0.0132 ± 0.0231 and -27.7 ± 8.2 deg., respectively, where the deviations are probable errors.

TABLE IV^a

CARBON-HYDROGEN VIBRATIONAL FREQUENCIES OF *cis*-DIBROMOETHYLENE AND MALEIC ANHYDRIDE

	$\text{C}_2\text{H}_2\text{Br}_2$		$\text{C}_2\text{D}_2\text{Br}_2$		ω_H/ω_D	$\text{C}_4\text{H}_2\text{O}_3$	$\text{C}_4\text{D}_2\text{O}_3$	ω_H/ω_D
	Infrared	Raman	Infrared	Raman		Infrared	Infrared	
Symmetric C-H stretch	3070	3085	..	2312	1.34	3120	2360	1.32
Asymmetric C-H stretch	..	3059	2291	2282	1.34	(2995) ^b	2330	1.29
Symmetric CHX in-plane bend	1147	1147	819	819	1.40	1060	766	1.38
Asymmetric CHX in-plane bend	1254	1248	993	993	1.26	1290	953	1.35
Symmetric C-H out-of-plane bend	671	..	517	515	1.30	696	518	1.34
Asymmetric C-H out-of-plane bend	..	866	..	679	1.28	842	680	1.24

^a Frequencies are in cm.^{-1} . ^b See reference 14b.

Vibrational Frequencies.—Examination of maleic acid-2,3- d_2 in the infrared revealed a spectrum too difficult for simple elucidation of the various modes. However the isotopic shifts observed in maleic anhydride- d_2 seem to be similar to that observed in the known spectra of *cis*-dibromoethylene- d_2 ¹⁴; both of these molecules belong to the C_{2v} group. The carbon-hydrogen vibrational modes of maleic anhydride were deduced by comparison with the spectra of *cis*-dibromoethylene and are shown in Table IV. The spectra are shown in Fig. 1. By assuming that the carbon-hydrogen vibrational frequencies in maleic anhydride are not too different from those in maleic acid, treatment of the observed isotope effect data can be attempted.

(14) (a) J. M. Dowling, P. G. Puranik, A. G. Meister and S. I. Miller, *J. Chem. Phys.*, **26**, 233 (1957); (b) see also L. Kahovec and K. W. F. Kohlrausch, *Z. Elektrochem.*, **43**, 282 (1937), for the Raman spectrum of maleic anhydride; (c) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Ed., Methuen and Co., Ltd., London, 1959, p. 34.

In order to evaluate $(\omega_{H_i} - \omega_{D_i}^\ddagger)$ from the slope, it is necessary to calculate a weighted average r_i . The frequencies for tetrahedral C-H are assumed to be the same as those chosen by Streitwieser, *et al.*² In the ground state, there are three pairs of sp^2 -hybridized carbon-hydrogen frequencies where only one of each pair changes to the tetrahedral carbon-hydrogen frequencies. For lack of more exact data the average of each pair is taken as the ground state frequencies. The changes in vibrational frequencies accompanying the conversion to a fully formed tetrahedral carbon are 3058 to 2890 cm.^{-1} , 1175 to 1340 cm.^{-1} and 769 to 1340 cm.^{-1} or a total net change of about 565 cm.^{-1} . The weighted average r_i , obtained from Table IV, is then 1.31. Substituting the common values for h , c and k into the expression for the slope and using r_i equal to

(15) J. Bigeleisen and M. Wolfsberg in "Advances in Chemical Physics," Vol. I, I. Prigogine, Editor, Interscience Publishers, Inc., New York, N. Y., 1958, p. 20.

1.31, the experimentally determined net total change in frequencies in going from the ground state to transition state is $375 \pm 111 \text{ cm.}^{-1}$. The experimentally measured change is a little more than half of the 565 cm.^{-1} total change.

Badger¹⁶ has devised rules relating the stretching force constant to the equilibrium distance between two atoms. Equation 19, where k is the

$$1/\sqrt{k} = a_{ij}(D_e - b_{ij}) \quad (19)$$

force constant, a_{ij} and b_{ij} are constants depending on the nature of the atoms involved, and D_e is the equilibrium internuclear distance, is valid for the normal as well as the excited states of molecules. Since the frequency of vibration is directly proportional to the square root of the force constant, the internuclear distance is then inversely proportional to the frequency. A set of rules, having the same form, have not, as yet, been shown to be valid for bending frequencies. However, if it is assumed that a similar relationship exists for bending frequencies (in this case, as the carbon-sulfur bond length decreases the carbon-hydrogen bending frequency increases), then one might position the transition state as lying a little more than halfway

(16) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934); **3**, 710 (1935).

between the ground state and a fully formed tetrahedral carbon atom having a normal carbon-sulfur bond length.

Now that frequency increments have been determined the $(1 - e^{-u})$ terms can be evaluated. If both the in-plane and out-of-plane bending frequencies are used and calculated separately for 15 and 80°, the products of the ratios are 1.025 and 1.035, respectively. This term changes relatively little in this temperature range and an average value of 1.030 for C can be used to evaluate $(\nu_{\text{H,L}}^{\pm}/\nu_{\text{D,L}}^{\pm})$. The antilogarithm of the intercept is 1.032 ± 0.05 so the ratio of the imaginary frequencies along the reaction coordinate is essentially 1.00 ± 0.05 as expected.¹ Calculation of this term using reduced masses of the fragments involved¹⁷ leads to 1.003. The data are in agreement but unfortunately not precise enough to verify the theoretical calculation of the ratio of imaginary frequencies along the reaction coordinate.

Acknowledgments.—I wish to thank Drs. A. J. Kresge, R. E. Weston, Jr. and M. Wolfsberg for helpful discussions during the course of this investigation. I would also like to acknowledge the mass spectral analysis by Mr. T. H. Middleton and the combustion of samples by Mrs. C. Paul.

(17) Ref. 15, p. 30.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY, BALTIMORE 18, MARYLAND]

Electron Spin Resonance of Copper Phthalocyanine^{1a}

BY E. M. ROBERTS^{1b} AND W. S. KOSKI

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The electron spin resonance spectrum of copper phthalocyanine in sulfuric acid was studied at low temperatures. The nitrogen hyperfine structure was observed, and it was found that the nitrogen splitting was smaller in the region near H_{\parallel} than the splitting in the H_{\perp} region. An explanation for this observation is proposed and a bonding parameter reflecting the nature of the copper-nitrogen bond is evaluated. The values of g_{\parallel} and g_{\perp} were determined as 2.180 and 2.037, respectively.

Introduction

A few years ago the paramagnetic resonance of crystalline copper phthalocyanine was reported.² Although the copper hyperfine structure was observed, no evidence of the nitrogen hyperfine structure appeared. It was supposed that the absence of nitrogen hyperfine structure was due either to poor resolution and the small magnetic moment of nitrogen or to a copper-nitrogen bond of high ionic character. Recently we have observed the nitrogen hyperfine structure in copper etioporphyrin II when the compound is dissolved in a suitable solvent such as benzene.³ It was therefore of interest to re-examine the phthalocyanine problem and this report is a summary of our results.

(1) (a) This investigation was supported in part by research grant RG-5144 from the division of General Medical Science, Public Health Service, National Institutes of Health. (b) Socony Mobil Field research, Dallas, Texas.

(2) J. F. Gibson, D. J. E. Ingram and D. Schonland, *Discussions Faraday Soc.*, **26**, 72 (1958).

(3) E. M. Roberts and W. S. Koski, *J. Am. Chem. Soc.*, **82**, 3006 (1960).

Experimental

The electron spin resonance measurements were made with a Varian model V 4500 epr spectrometer utilizing 100 kc. modulation. The magnetic field was monitored with a Harvey-Wells Model 501 nuclear magnetic resonance gaussmeter. Each spectrum was generally preceded by a spectrum of a benzene solution of DPPH. All measurements of the copper phthalocyanine were made on 0.001 molar solutions in concentrated sulfuric acid. The value of g_{\parallel} could be readily evaluated from the observed spectrum; however, difficulty was experienced in evaluating g_{\perp} because of the overlap of the two patterns. The value of g_{\perp} was obtained therefore from polycrystalline samples using the procedure outlined by Sands⁴ and Kneubühl.⁵

Results and Discussion

Figure 1 shows a typical spectrum of sulfuric acid solution of copper phthalocyanine at -137° . This spectrum is very similar to the spectrum of copper etioporphyrin II in castor oil,³ and it will be noted that the nitrogen hyperfine structure is readily observable. In each case the total spread

(4) R. H. Sands, *Phys. Rev.*, **99**, 1222 (1955).

(5) F. K. Kneubühl, *J. Chem. Phys.*, **33**, 1074 (1960).