[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY]

The Dipole Moment of Thioacetoacetic Ester in Solution[1]

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Values of the apparent dipole moment of 2.2 to 2.4 *D* were observed for thioacetoacetic ester dissolved in benzene, *n*-hexane, carbon tetrachloride and carbon disulfide. Structural configurations have been assigned to the thioenol and thione tautomeric forms of the ester and their dipole moments calculated from reported bond and group moments. On the basis of the observed and calculated values, it is postulated that a *trans*-thione and a *trans*-thioenol tautomer with the latter exhibiting intramolecular rotation are the predominant configurations of the ester in solution.

Introduction

In conjunction with a study comparing the metal chelate complexes containing sulfur with those containing oxygen,[2] it was found desirable to investigate the structure of certain sulfur compounds. The present paper reports the results of a study of the structure of thioacetoacetic ester dissolved in non-polar solvents as determined by dielectric constant measurements.

Structural investigations on the analogous oxygen compound, acetoacetic ester, have been relatively extensive.[3] It has been established that there are two tautomeric forms, the enol and keto, existing in equilibrium with the former present as a chelate. The equilibrium constant varies with the polarity of the solvent as predicted by the van't Hoff-Dimroth relationship.[4] Le Fèvre and Welsh[5] have shown that the measured dipole moment of acetoacetic ester obeys the mixture law.

Thioacetoacetic ester also exists in two tautomeric forms,[6] namely, the thione and thioenol. Mitra[7] has determined the per cent. of the thioenol form in solutions of ethyl alcohol, but no results have been reported concerning the effect of solvent variation on the equilibrium constant.

It was felt that the determination of the dipole moment of thioacetoacetic ester in solution would furnish quantitative information concerning the system, without altering the equilibrium between the two tautomeric forms during the measurements.

Experimental Procedure

A. **Apparatus.**—An alternating current heterodyne beat apparatus[8] was employed to measure the dielectric constants of the solutions at a frequency of 550 kilocycles per second by means of the parallel substitution method. A General Radio Co. Type 722-D Precision Condenser was chosen as the standard condenser. The liquid measuring cell[9] was calibrated with air and benzene. The dielectric constant of benzene was taken as 2.2730 at 25°.[10]

The refractive indices were measured with a Spencer Abbe type refractometer. Densities were determined with a glass pycnometer designed by Lipkin, *et al.*[11] All measurements were performed at 25.00 ± 0.01°.

B. **Solvents.**—High quality grades of benzene, *n*-hexane, carbon tetrachloride and carbon disulfide were purified by standard procedures. The benzene was dried over sodium and fractionally distilled. *n*-Hexane was extracted with sulfuric acid, washed with 10% NaOH and 1 *N* $KMnO_4$ mixtures, dried over anhydrous Na_2SO_4, and fractionally distilled. The carbon tetrachloride was dried over anhydrous Na_2SO_4. Carbon disulfide was distilled from a water solution and dried with anhydrous Na_2SO_4.

PHYSICAL PROPERTIES MEASURED

Solvent	$d_{25}/_{25}$	$n^{25}D$	ϵ_{25}
Benzene	0.87322	1.4977	
n-Hexane	0.68509		1.9186
CCl_4	1.5850	1.4574	2.2272
CS_2	1.2574		2.6296

C. **Solutes.** 1. **Thioacetoacetic Ester.**—The ester was prepared by the method of Mitra.[12] Upon the addition of an alcoholic solution or suspension of a lead salt to an alcoholic solution of the ester, the orange mercaptide precipitated. It was separated, washed and suspended in alcohol. Hydrogen sulfide was passed through to liberate the free ester. The insoluble sulfide was filtered and the alcohol removed under reduced pressure. The orange-red ester was distilled under reduced pressure in an inert atmosphere.

Similar procedures were applied to the brown silver mercaptide and the yellow mercury mercaptide. In all cases, the ester distilled over a range depending on the rate of heating, *e.g.*, 70–81° (3 mm.). The failure of the lead mercaptide to yield an ester of constant boiling point has previously been reported[13] as due to the presence of isomers.

For the first three solvents employed, a sample of ester was used having the constants: $d_{25}/_{25}$ 1.0802, $n^{25}D$ 1.4937, R_D 39.38.

A sample of ester was employed for the carbon disulfide solutions having the physical properties: $d_{25}/_{25}$ 1.0621, $n^{25}D$ 1.4798, R_D 39.09. Literature values are: $d_{31}/_4$ 1.0554, $n^{26}D$ 1.4712 (Mitra); $d_{29.5}/_4$ 1.0747, n_D 1.53749 (Scheibler).

Assuming the same optical exaltation in β-mercaptocrotonic ester as in β-ethoxycrotonic ester, and choosing R_D 43.75 for the latter compound[14] as well as the bond refractivities of Vogel,[15] the calculated molar refractivities are: 100% thioenol, R_D 40.43; 100% thione, R_D 40.04.

2. **Methyl *o*-Mercaptobenzoate.**—A sample was obtained through the generosity of Dr. B. B. Speiser of the Medical Chemicals Corporation of Chicago, Illinois. The ester was distilled under reduced pressure in an inert atmosphere. The boiling point was 98–100° (2 mm.), $d_{25}/_{25}$ 1.2226, $n^{25}D$ 1.5911, R_D 46.50.

Results

The reported dielectric constants in Tables I and III represent the average of a minimum of four readings with a precision measure of 1 or 2 parts per thousand.

The values of the molar polarization of the solutes at infinite dilution (${}_\infty P_2$) were calculated by the

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(1) Presented at the Atlantic City Meeting of the A.C.S., September, 1952.

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(3) G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, Chapt. 14, p. 580.

(4) *Ibid.*, p. 607.

(5) R. J. W. Le Fèvre and H. Welsh, *J. Chem. Soc.*, 1909 (1949).

(6) S. K. Mitra, *J. Indian Chem. Soc.*, **8**, 471 (1931).

(7) *Ibid.*, **15**, 205 (1938).

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TABLE I

Solute, Thioacetoacetic Ester

f_2	ϵ_{12}	d_{12}	f_2	ϵ_{12}	d_{12}
Solvent, benzene, P_1 25.14_4			Solvent, hexane, P_1 29.48_2		
0.00000	2.2730	0.87322	0.00000	1.9186	0.68509
.00125	2.2832	.87346	.00187	1.9268	.68577
.00538	2.3156	.87466	.00399	1.9357	.68672
.01031	2.3457	.87609	.00788	1.9543	.68826
.02184	2.4431	.87949	.01611	1.9923	.69192
Solvent, CCl_4, P_1 26.77_6			Solvent, CS_2, P_1 21.04_4		
0.00000	2.2272	1.5850	.00000	2.6296	1.2574
.00155	2.2379	1.5842	.00092	2.6365	1.2572
.00611	2.2654	1.5811	.00186	2.6455	1.2567
.01211	2.3021	1.5767	.00364	2.6715	1.2547
.02274	2.3704	1.5691	.00636	2.6962	1.2541
			.00906	2.7175	1.2524
			.01336	2.7632	1.2501

TABLE II

Solvent	ϵ_1	v_1	α	β	$_\infty P_2$	μ, D
Benzene	2.2732	1.1455	7.88	−0.398	156.47	2.38
CCl_4	2.2272	0.63082	6.25	.282	141.17	2.22
Hexane	1.9172	1.4595	4.66	− .881	146.78	2.28
CS_2	2.6282	0.79502	9.98	.371	135.42	2.16

method of Halverstadt and Kumler[16] employing the expression

$$_\infty P_2 = \frac{3\alpha v_1 M_1}{(\epsilon_1 + 2)^2} + (M_2 v_1 + M_1 \beta)\frac{(\epsilon_1 - 1)}{(\epsilon_1 + 2)} \quad (1)$$

ϵ_{12}, the dielectric constants and v_{12} the specific volumes of the solutions were plotted against f_2, the mole fractions of the solute. ϵ_1 and α, the intercept and slope of the ϵ_{12} *vs.* f_2 functions, and v_1 and β, the corresponding properties of the v_{12} *vs.* f_2 functions, were calculated. The quantities M_1 and M_2 are the molecular weights of the solvent and solute, respectively.

The apparent dipole moments of the two solutes in Debye units were calculated by the Debye equation

$$\mu = 0.01273\sqrt{(_\infty P_2 - P_D)T} \quad (2)$$

The value of P_D, the distortion polarization, was chosen as R_D, the molar refraction for the NaD line.

Measured and calculated quantities for the thioacetoacetic ester systems and the methyl *o*-mercaptobenzoate system are listed in Tables I–III. The quantity P_1 recorded in Table I is the value of the molar polarization determined by the measured value of ϵ for hexane, carbon tetrachloride and carbon disulfide and by the measured value of the refractive index for benzene.

TABLE III

Solute, Methyl *o*-Mercaptobenzoate; solvent, benzene

f_2	ϵ_{12}	d_{12}		
0.00000	2.2730	0.87322	ϵ_1	2.2782
.00175	2.2926	.87378	v_1	1.1448
.00741	2.3380	.87717	α	8.81
.01447	2.3971	.88006	β	−0.582
.02586	2.4896	.88503	αP_2	173.08
			μ, D	2.47

The values of the dielectric constants of benzene, hexane and carbon disulfide calculated from the ϵ_{12} *vs.* f_2 functions agree well with those reported in the literature,[17] and in the case of carbon tetrachloride the two are identical.

Figure 1 contains several possible models of the tautomers of thioacetoacetic ester. A and B are thione whereas C-F are thioenol configurations. The covalent bond and van der Waals radii listed by Pauling[18] have been employed for their construction. The ethoxy group was assigned a *cis* configuration.[19] Table IV lists the values of the calculated moments determined by the bond and group moments compiled by Smyth[20] and the following bond angle assignments: ∢ CSH = 113°, ∢ COC = 113°,[19] angles about a double bond carbon = 120°, and all other carbon bond angles = 109°.

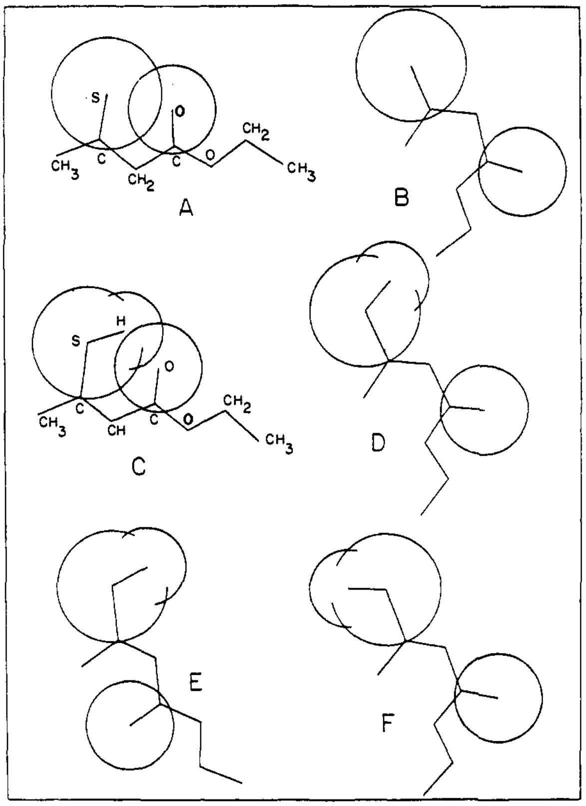

Fig. 1.

TABLE IV

Structure	A	B	C	D	E	F
Calcd. moment	4.81	2.64	3.93	1.17	2.42	2.42

The group moment of CH_3CS– has been taken as 3.04 D with its resultant acting at an angle of 58° to the carbon of the group attached. This value was obtained by adding 0.3 D (difference between C=O and C=S bond moment) to the CH_3CO– group moment given by Smyth.[21] The

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group moment of $-COOC_2H_5$ was taken as 1.86 *D*, the measured value of ethyl acetate, with its resultant acting at an angle of 73° to the carbon of the group attached. This latter angle was calculated from the measured moment of diethyl oxalate,[22] 2.49 *D*.

Discussion

One might expect that the structure of the thione tautomer as given by A is more probable than B since it contains the generally accepted zig-zag carbon skeleton configuration. Smyth,[22] however, has proposed a ring structure of type B for diethyl succinate. There are factors in operation which make the *trans* configuration B more likely.

First, configuration B has a calculated moment of 2.6 *D* in contrast to the calculated value of 4.8 *D* for the *cis* form A. Since the observed moments of the ester lie between 2.2 and 2.4 *D* it is more likely that structure B prevails as the thione modification. Second, an examination of the Fisher–Hirschfelder atomic models and the molecular diagrams clearly indicates less steric hindrance for the *trans* configuration. Third, the sulfur and oxygen atoms would most favorably be oriented in that position giving a minimum resultant moment.

Of the thioenol configurations C–F, the *trans* forms D, E and F may be considered more likely than the *cis* C for several reasons. Less relative intramolecular rearrangement is associated with the transformation of the *trans* thione configuration to the *trans* thioenol than to the *cis* thioenol structure. Also, as in the previous case, the *cis* modification exhibits greater steric hindrance. In acetoacetic ester, the larger steric hindrance and the usually larger moment of the *cis* configuration are compensated by stabilization through hydrogen bonding. In thioacetoacetic ester, however, this is not probable since there is little evidence for the presence of hydrogen bonds between the sulfhydryl group and oxygen.[23]

It is possible that the thioenol tautomer is a *trans* modification exhibiting intramolecular rotation for which D, E and F represent specific configurations. The value of the resultant moment of this structure can be identified with that of methyl *p*-mercaptobenzoate since they have the same relative configurations.

Angyal and Le Fèvre[24] have shown that ethyl salicylate and ethyl *p*-hydroxybenzoate have essentially the same moments, 2.81 and 2.71 *D*, respectively. The corresponding acids also have similar moments, 2.63 and 2.73 *D*, respectively.[25]

Since methyl *o*-mercaptobenzoate was available in this Laboratory but not the *p*-compound, the moment of the latter was taken as that measured for the *o*-compound in benzene, 2.47 *D*.

The observed narrow range of 2.2 to 2.4 *D* for the moment of thioacetoacetic ester in non-polar solvents can be interpreted as evidence for the presence of a *trans*-thioenol tautomer exhibiting intramolecular rotation and a *trans*-thione tautomer whose moments are 2.5 and 2.6 *D*, respectively.

From the work of Le Fèvre and Welsh[5] it might be expected that the law of mixtures is obeyed by thioacetoacetic ester, namely

$$\mu^2 = f_E\,(\mu_E^2 - \mu_K^2) + \mu_K^2 \qquad (3)$$

a minimum value for the moment of the thione form μ_K may be estimated by assuming that the moment of the thioenol form μ_E is 2.5 *D* and by choosing the thioenol content in *n*-hexane as 63%. The enol content of acetoacetic ester in *n*-hexane is 63%,[5] and it is likely that a larger amount of enol than thioenol is present in a non-polar solvent.[26] A value of μ_K of 1.91 *D* is obtained. Similarly, a maximum value of 2.28 *D* is estimated by choosing a safe minimum value of 10% as the thioenol content. The values of the moments thus estimated for the thione form are more close to the value calculated for structure B than that of A.

Although unpublished work of the authors indicates that metal chelates are formed with thioacetoacetic ester which is presumably in the *cis*-thioenol modification, this does not conflict with the conclusions reached in this paper since metals are known to shift the *trans*-enol to the *cis*-enol configurations in the case of the oxygen analogs.[27]

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