

Dielectric Polarization Measurements on Some β -Diketones & β -Ketoesters in Solution : Part I—Ethyl Acetoacetate

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The apparent solution moments of ethyl acetoacetate in various solvents have been measured. In certain solvents, practically linear relationship has been observed between the square of this moment and the corresponding mole percentage of each tautomer. Probable dipole moments and conformations of the keto and enol molecules together with their relative proportions in various media have been inferred from dipole moment measurements of the ester under limiting cases. In other solvents, solute-solvent interactions through hydrogen bonding or dipole forces have been suggested.

Dielectric polarization measurements were first used by Le Fevre and Welsh¹ for the investigation of the keto-enol equilibrium of ethyl acetoacetate in some non-polar and polar solvents, for which the usual Debye² equation was applied. However, these results were later considered inconclusive in a re-investigation by Le Fevre *et al.*³ Hence, in view of such uncertainties, it seemed worthwhile to investigate in the present series of work the following aspects:

(i) the effects of some non-polar solvents on the keto-enol equilibria of some β -diketones and β -ketoesters, first in very dilute solutions by determining the apparent solution moment, μ_{obs} , using the usual Debye² equation, and secondly at various concentrations throughout the whole range by determining the corresponding moment, μ_2 , using the modified⁴ form of the Onsager⁵ equation;

(ii) the effects of some polar solvents on the above equilibria by measuring the apparent solution moment of the ester at infinite dilution, $(\mu_2)_{f \rightarrow 0} = \mu_{\text{obs}}$, using another form⁶ of the Onsager⁵ equation;

(iii) whether the above measured dipole moments of the diketones or Ketoesters at infinite dilution in non-polar and polar solvents, i.e. μ_{obs} , together with the Onsager⁵ dipole moment, $S^{1/2}\mu_0$, and the Kirkwood⁷ dipole moment, $g^{1/2}\mu_0$, of the pure ester can be related to the corresponding positions of the tautomeric equilibria;

(iv) evaluation of specific interactions in a given solvent from measurement of the apparent solution moment at infinite dilution in that solvent, compared with that in an inert, non-polar solvent;

(v) in the absence of such interactions, use of the curve drawn to express the relation between square of the measured moment, in various solvents at infinite dilution for a given temperature, and the corresponding enol mole fraction in the same solvent, as a

calibration curve for the determination of the equilibrium keto-enol ratios; and

(vi) use of this relation to infer the most probable conformations of the keto and enol molecules in view of the deduced values of their dipole moments.

This paper is concerned with the investigation of the above mentioned aspects in the keto-enol tautomerism of ethyl acetoacetate.

Materials and Methods

Ethyl acetoacetate (BDH) was dried using CaCl_2 , filtered, and then distilled. The middle fraction was collected. The solvents cyclohexane, dioxan, carbon tetrachloride, benzene, chloroform, triethylamine, and acetone were purified by standard procedures^{8,9}. Solutions were prepared by weight, and left overnight at room temperature to equilibrate before carrying out any measurements.

Measurements of density, refractive index, and dielectric constant, and calculations of the apparent solution moments at the condition of infinite dilution, μ_{obs} , and at various concentrations, μ_2 , were made as previously described^{6,10,11}. On the other hand, the equilibrium ratio of the two tautomers in dilute solutions of the ester in cyclohexane, dioxan, carbon tetrachloride, and chloroform was determined at 25°C by the analysis of the ultraviolet¹² absorption spectra, whereas the values of this ratio in the other solvents and in the pure condensed and vapour phases of the ester were taken from literature^{1,3,13,14}.

Results

In Table 1 the following data are listed:

(i) The values we obtained for the apparent solution moments of ethyl acetoacetate at infinite dilution, μ_{obs} , in non-polar and polar solvents at 25 to 50°C.

Table 1—Dipole Moments and Enol Mole Per Cent of Ethyl Acetoacetate in Various Solvents

Solvent	$\mu_{\text{obs.}}$				Mole % enol (25°C)	Method	Reference
	25°	30°	40°	50°C			
Cyclohexane	2.50	2.56	2.59	2.62	62.4	UV	present work
Dioxane	3.02	3.04	3.06	3.08	29.0	UV	present work
CCl ₄	2.91	2.92	2.94	2.96	36.8	UV	present work, (3)
Benzene	2.87	2.88	2.90	2.97	15.7	NMR	(3)
Chloroform	—	3.82	3.81	3.72	7.0	UV	present work
Triethylamine	2.70	2.80	2.87	2.94	100.0	—	—
Acetone	3.21	3.22	—	—	7.3	Bromine	(12)
Gas	2.93	(121-58°C)	—	(15)	39.0	—	(13)
Liquid							
$S^{1/2}\mu_0$	3.35	3.36	3.36	3.36			
$g^{1/2}\mu_0$	3.39	3.40	3.40	3.40	7.4	Bromine	(12)

(ii) The calculated Onsager $S^{1/2}\mu_0$ and Kirkwood $g^{1/2}\mu_0$ moments of the pure ester at 25 to 50°C.

(iii) The enol mole percentages determined by various authors^{1,3,13,14} and in the present work.

(iv) The vapour moments of the ester¹⁵ over the temperature range 121-158°C.

Figure 1 shows the relation between the measured μ^2 of the ester in various solvents at infinite dilution as well as in vapour and condensed phases, and the corresponding enol mole fraction N_{enol} . Detailed data required for the determination of the apparent solution moments of the ester in non-polar and polar solvents, μ_{obs} , are shown in Tables 2 and 3, respectively.

Finally as a representative example, Fig. 2 shows the variation of the square of the dipole moment of the ester, μ_2^2 , with the mole fraction, f_2 , in cyclohexane.

Discussion

In the absence of specific interactions in very dilute solutions of ethyl acetoacetate in various solvents, a plot of the square of the apparent solution moment at infinite dilution, μ_{obs}^2 , against the enol mole fraction, N_{enol} , under the same condition, is expected to be linear on the basis of the simple mixture formula. In Fig. 1, points representing measurements at 25°C in cyclohexane, dioxan, carbon tetrachloride, and in pure condensed and vapour phases and in acetone, suggest that a straight-line relation is not incorrect. However, the remaining three points corresponding to measurements in chloroform, triethylamine, and benzene obviously deviate from the straight-line relation. Hence, the former six points have been utilized to draw the best linear relationship between μ^2 and N_{enol} at 25°C. The equation thus obtained for this line is,

$$\mu^2 = 11.49 - 7.92 N_{\text{enol}} \quad \dots(1)$$

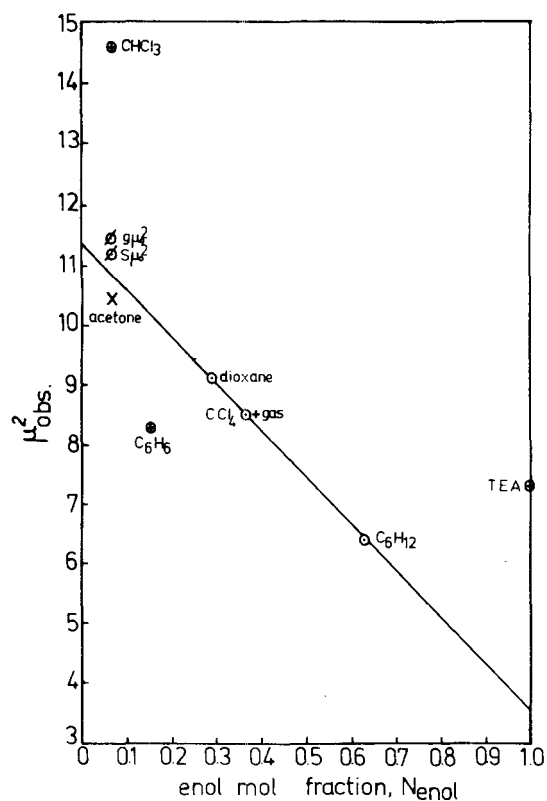


Fig. 1—Relation between the square of the measured dipole moment of ethyl acetoacetate in various solvents at infinite dilution at 25°C and the corresponding enol mole fraction.

where μ is expressed in Debye units. Accordingly, $\mu_{\text{keto}} = 3.39$ D, and $\mu_{\text{enol}} = 1.89$ D.

It is interesting to compare the difference $\mu_{\text{keto}}^2 - \mu_{\text{enol}}^2 = 7.92$ D² with that obtained by other authors¹⁶ from other lines of evidence. Based on the Onsager-Kirkwood^{5,7} model, Powling and Bernstein¹⁶ developed the following equation:

Table 3—Apparent Solution Moments of Ethyl Acetoacetate in Polar Solvents

$w_2 \times 10^2$	$t(^{\circ}\text{C})$	ϵ_{12}	d_{12}	C_2
<i>Acetone</i>				
0	20	21.3105	0.7909	0
	25	20.7973	0.7866	0
	30	20.2706	0.7814	0
2.0893	20	21.2426	0.7953	0.1277
	25	20.7973	0.7895	0.1267
	30	20.2347	0.7849	0.1260
4.0762	20	21.1773	0.7985	0.2501
	25	20.6762	0.7934	0.2485
	30	20.1828	0.7889	0.2471
6.0432	20	21.1126	0.8033	0.3730
	25	20.6006	0.7975	0.3703
	30	20.1002	0.7927	0.3681
7.9991	20	21.0299	0.8068	0.4959
	25	20.5474	0.8017	0.4927
	30	20.0425	0.7964	0.4895

$t(^{\circ}\text{C})$	n_{1-D}^2	$\mu_1 \times 10^{18}$	C_1°	$(d\epsilon_{12}/dC_2)_{C_1 \rightarrow 0}$	$(F)_{C_1 \rightarrow 0}$	$\mu_2 \times 10^{18}$
20	1.8423	2.85	13.6250	-0.5586	0.9533	3.18
25	1.8360	2.85	13.5513	-0.5145	0.9419	3.21
30	1.8290	2.85	13.4620	-0.4833	0.9510	3.22

$w_2 \times 10^3$	$t(^{\circ}\text{C})$	ϵ_{12}	d_{12}	$C_2 \times 10^2$
<i>Chloroform</i>				
0	30	4.6322	1.4706	0
	40	4.4646	1.4508	0
	50	4.3031	1.4320	0
2.9534	30	4.6575	1.4682	3.3318
	40	4.4781	1.4489	3.2881
	50	4.3294	1.4304	3.3246
6.1856	30	4.7201	1.4660	6.9675
	40	4.5424	1.4470	6.8776
	50	4.3801	1.4286	6.7898
9.1345	30	4.7797	1.4639	10.2749
	40	4.5999	1.4453	10.1442
	50	4.4361	1.4269	10.0153
15.2414	30	4.9030	1.4598	17.0953
	40	4.7138	1.4417	16.8841
	50	4.5604	1.4235	16.6712

$t(^{\circ}\text{C})$	n_{1-D}^2	$\mu_1 \times 10^{18}$	$(d\epsilon_{12}/dC_2)_{C_1 \rightarrow 0}$	$(F)_{C_1 \rightarrow 0}$	$\mu_2 \times 10^{18}$
30	2.0699	1.15	1.7839	0.8323	3.82
40	2.0526	1.15	1.6983	0.8308	3.81
50	2.0335	1.15	1.5410	0.8295	3.72

$w_2 \times 10^3$	$t(^{\circ}\text{C})$	ϵ_{12}	d_{12}	$C_2 \times 10^2$
<i>Triethylamine</i>				
0	25	2.4200	0.7234	0
	30	2.3933	0.7170	0
	40	2.3521	0.7068	0
	50	2.3170	0.6967	0
4.5490	25	2.4380	0.7244	2.5321
	30	2.4164	0.7187	2.5122
	40	2.3684	0.7084	2.4762
	50	2.3158	0.6984	2.4411
	25	2.4459	0.7248	3.2825
	30	2.4242	0.7192	3.2576

—Contd.

Table 3—Apparent Solution Moments of Ethyl Acetoacetate in Polar Solvents—(Contd.)

$w_2 \times 10^3$	$t(^{\circ}\text{C})$	ϵ_{12}	d_{12}	$C_2 \times 10^2$
<i>Triethylamine—Contd</i>				
5.8945	40	2.3853	0.7089	3.2108
	50	2.3458	0.6989	3.1645
	25	2.4568	0.7256	4.5005
8.0721	30	2.4348	0.7211	4.4723
	40	2.3940	0.7111	4.4106
	50	2.3537	0.7009	4.3473
11.3250	25	2.4705	0.7263	6.2320
	30	2.4508	0.7219	6.2815
	40	2.4086	0.7119	6.1944
15.7405	50	2.3713	0.7016	6.1049
	25	2.4925	0.7269	8.7916
	30	2.4698	0.7228	8.7422
	40	2.4262	0.7122	8.8133
	50	2.3846	0.7022	8.4932

$t(^{\circ}\text{C})$	n_{D}^2	$\mu_1 \times 10^{18}$	C_1°	$(d\epsilon_{12}/dC_2)_{C_2 \rightarrow 0}$	$(F)_{C_2 \rightarrow 0}$	$\mu_2 \times 10^{18}$
25	1.9533	0.66	7.1491	0.8332	0.8281	2.70
30	1.9438	0.66	7.0861	0.8787	0.8286	2.80
40	1.9296	0.66	6.9853	0.8841	0.8296	2.87
50	1.9152	0.66	6.8856	0.8935	0.8310	2.94

$$\Delta H_{\text{solution}} = \Delta H_{\text{gas}} - \left(\frac{\epsilon - 1}{2\epsilon + 1} \frac{d}{M} \right)_{\text{solvent}} \times (\mu_{\text{enol}}^2 - \mu_{\text{keto}}^2) \times \text{constant} \quad \dots(2)$$

where $\Delta H_{\text{solution}}$ and ΔH_{gas} are the heats of enolization of the ester at infinite dilution in the non-polar or slightly polar solvents and in the gas phase, respectively, and $\left(\frac{\epsilon - 1}{2\epsilon + 1} \frac{d}{M} \right)$ is a solvent property.

Thus, equating the constant to $4\pi N^2/3$, where N is Avogadro's number, and assuming that ΔH is expressed in cal/mol, the slope of the line obtained by Powling and Bernstein on plotting $\Delta H_{\text{solution}}$ against the solvent property is given by:

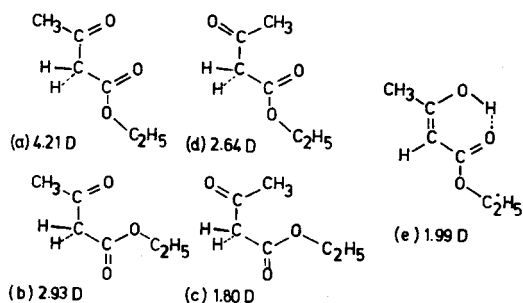
$$1.52 \times 10^{48} (\text{molecule/mol})^2 \times (\mu_{\text{keto}}^2 - \mu_{\text{enol}}^2) - (\text{dyne}^{1/2} \text{cm}^2/\text{molecule})^2 / 4.18 \times 10^7 (\text{erg/cal})$$

An estimated value of 8.14 D^2 for the difference $\mu_{\text{keto}}^2 - \mu_{\text{enol}}^2$ is evidently in satisfactory agreement with the value 7.92 D^2 obtained from dipole moment measurements.

On the other hand, the fact that Onsager and Kirkwood dipole moments calculated for pure liquid ester are practically identical (see Table 1) may lead one to suggest that neither self-association nor short-range forces, such as intermolecular hydrogen bonding, play an important rôle in the condensed phase of the ester, the magnitude of S and g factors being most likely in the close proximity of unity.

Furthermore, the most probable conformations of the keto and enol molecules can be inferred on the

basis of the deduced values of their dipole moments. Thus, shown below are the various conformations, together with the corresponding dipole moments calculated using the usual vector summation method of bond moments¹⁷.



Obviously, the most probable conformations of the keto and enol molecules are (b) and (e), respectively.

The pronounced normality of the solvents cyclohexane, carbon tetrachloride, and dioxan, as exhibited by the linear relation between μ_{obs}^2 and N_{enol} also signifies that interactions of the types keto-keto, enol-enol, and keto-enol are insignificant in the ester, and that the shift in the keto-enol equilibrium on dilution with these solvents, is caused by change in dielectric constant. If one assumes that this normality still holds in concentrated solutions, then it follows that Eq.(1) would be roughly suited to the determination of the keto-enol proportions over the whole range of concentrations from measured dipole

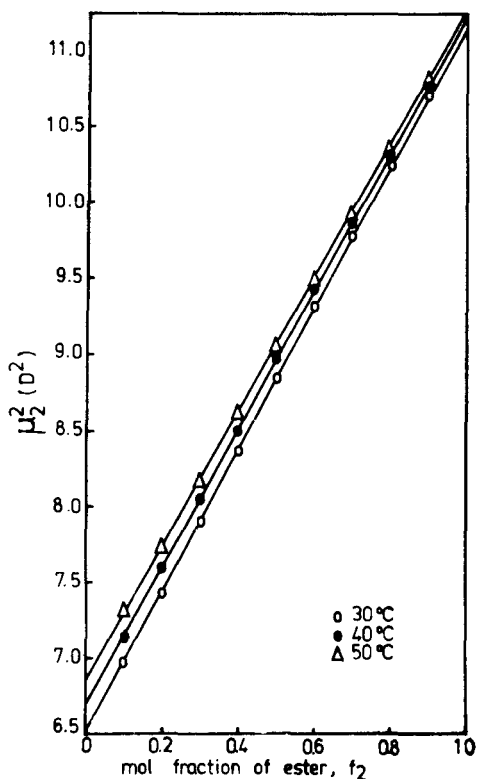


Fig. 2—Variation of the square of the dipole moment of the ester in cyclohexane with its mole fraction in cyclohexane

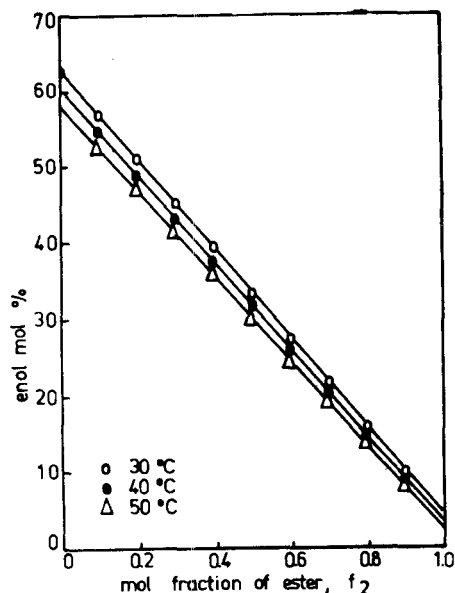


Fig. 3—Dependence of the enol mole per cent on the mole fraction of the ester in cyclohexane

moments. As a representative example cyclohexane has been chosen as the solvent. Thus, the measured dipole moment of ester at various concentrations (Fig. 2) was used to calculate from Eq. (1) the corresponding mole percentages of enol, as shown in Fig. 3 over the temperature range 30 to 50°C. Then from a plot of $\ln K_e$ against $1/T$ at each concentration, ΔH and ΔS of enolization were determined. The results obtained, together with those of ΔG° assuming normality, are represented in Figs 4 and 5, respectively. It will be evident from Fig. 4 that the enthalpy difference ($H_{\text{enol}} - H_{\text{keto}}$) of -2.16 kcal/mol between the two forms of ethyl acetoacetate at infinite dilution in cyclohexane is quite high compared with the value -1.48 obtained in the pure liquid. Perhaps the solvation of the enol isomer by cyclohexane lowers its energy by approximately one kcal/mol. It may be pointed out that our value of ΔH in cyclohexane is in fair agreement with that obtained (-1.8 kcal/mol) in hexane by Powling and Bernstein¹⁶, the enol mole percentages in these two solvents being practically the same (about 63%). On the other hand, the appreciable value of ΔS ($S_{\text{enol}} - S_{\text{keto}}$) which is -10.3 cal/mol/degree in the pure liquid conforms well to the ring structure of the enol form. That is, the greater the degree of order involved in the ring structure of this tautomer, more negative is the ΔS . However, the

increase in the value of ΔS from -10.3 (in pure liquid) to -6.04 cal mol⁻¹ degree⁻¹ at infinite dilution in cyclohexane may be associated with the entropy change of mixing, assuming, of course, that there are no molecular interactions.

The fact that the dissolution of the ester in the non-polar solvent benzene does not conform to the above normality (see Fig. 1) is indicative of molecular interactions. Interactions between the π -electrons of the two carbonyl groups in the keto form and the π -electron cloud in benzene, i.e. π - π interactions may be responsible for the deviation. Reference may be made here to the molar Kerr constant of the ester in benzene³, the negativity of which was accounted for by assuming that the keto form can loosely associate with benzene to produce complexes having increased polarizabilities in directions perpendicular to the resultant dipole moment.

Polar solvents are generally known to cause preferential solvation of the keto form owing to the highly localized polarities in their molecules as a consequence of which, they could confer to this tautomer by association¹ via antiparallel alignment of the dipole moments. This, however, is not the only factor affecting the equilibrium position between the two tautomers, since in addition, interactions might take place between the polar solvents and any of the two tautomers depending on the solvent.

A comparison between the dipole moment value of 3.82 D in chloroform with the value 3.29 D calculated from Eq. (1) considering enol mole percentage 7%¹³ might, therefore, suggest a preferential solvation of the keto molecules by chloroform followed by an

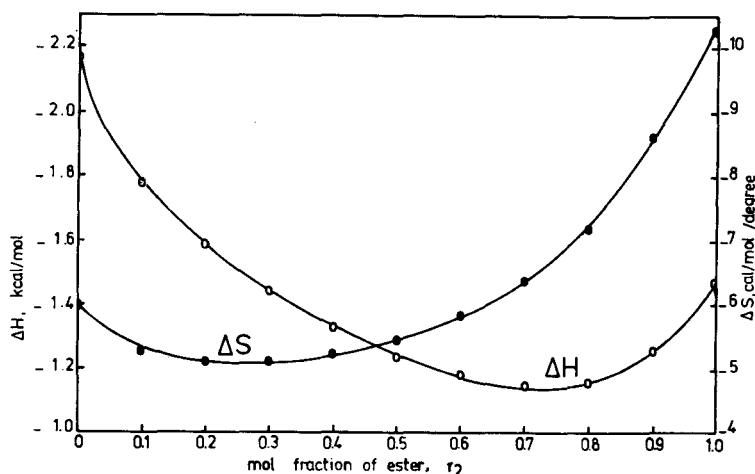

 Fig. 4—Enthalpy change (ΔH), and entropy change (ΔS) of enolization as a function of the mole fraction of ester in cyclohexane

Table 4—Apparent Solution Moment of Acetone in Chloroform

$w_2 \times 10^3$	$t(^{\circ}\text{C})$	ϵ_{12}	d_{12}	C_2
0	30	4.6322	1.4706	0
	40	4.4646	1.4508	0
	50	4.3031	1.4320	0
2.0716	30	4.7127	1.4681	0.0524
	40	4.5399	1.4485	0.0517
	50	4.3723	1.4295	0.0510
3.1227	30	4.7535	1.4668	0.0789
	40	4.5780	1.4473	0.0778
	50	4.4072	1.4283	0.0768
5.7532	30	4.8552	1.4637	0.1450
	40	4.6731	1.4443	0.1431
	50	4.4946	1.4251	0.1412
10.0186	30	5.0192	1.4586	0.2516
	40	4.8265	1.4395	0.2483
	50	4.6353	1.4200	0.2449
15.7452	30	5.2375	1.4517	0.3935
	40	5.0308	1.4331	0.3885
	50	4.8226	1.4131	0.3830

$t(^{\circ}\text{C})$	n_D^2	$\mu_1 \times 10^{18}$	C_1°	$(d\epsilon_{12}/dC_2)_{C_1 \rightarrow 0}$	$(F)_{C_1 \rightarrow 0}$	$\mu_2 \times 10^{18}$
30	2.0699	1.15	12.319	1.5385	0.8323	3.57
40	2.0526	1.15	12.153	1.4575	0.8308	3.55
50	2.0335	1.15	11.996	1.3563	0.8295	3.51

association of a co-operative type represented by $\text{Cl}_3\text{C}^{\oplus} \text{---} \text{H} \cdots \text{O}^{\ominus} \text{C}(\text{CH}_3)\text{CH}_2\text{COOC}_2\text{H}_5$, in which induced moments acting in the same direction are also involved. A rough estimate of such an interaction can be made by taking it as the difference between these two values, i.e. 0.52 D. A justification has been suggested by determining the dipole moment of acetone in chloroform at infinite dilution, the results obtained being shown in Table 4. The value 3.56 D signifies when compared with the gas value¹⁸ (2.97 D) that there are molecular interactions between acetone and chloroform, associated with a dipole moment of

0.59 D; a value which is in fair agreement with that deduced for ester-chloroform interaction.

Expectedly, the dissolution of ethyl acetoacetate in triethylamine would first result in enolization, arising from the lower dielectric constant ($\epsilon_{25} = 2.42$) of the solvent than that of the solute ($\epsilon_{25} = 15.7$). This enolization is then followed by a specific interaction of the nitrogen lone pair with the enolic proton leading to an intermolecular hydrogen bond: $(\text{C}_2\text{H}_5)_3\text{N} \cdots \text{H} \text{---} \text{OC}(\text{CH}_3) = \text{CHCOOC}_2\text{H}_5$. Hence, if we accept that at infinite dilution when complex formation is maximum, the ester is wholly in the enol form, then the

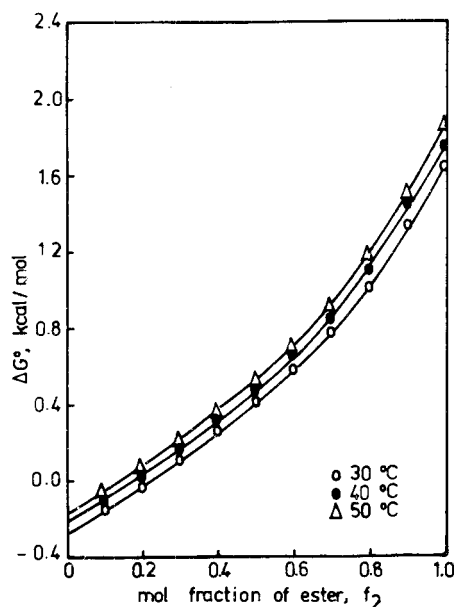


Fig. 5—Free energy change (ΔG°) of enolization as a function of the mole fraction of the ester in cyclohexane

difference between the measured dipole moment of the ester in triethylamine (2.80 D) and that inferred for the enol (1.89 D) (see Fig. 1) may be attributed to such an interaction.

Despite its high polarity, acetone differs from other polar solvents (chloroform and triethylamine) in exhibiting no specific interactions with ethyl acetoacetate, thus resembling in this respect the inert, non-polar solvents. At the same time, acetone deviates from non-polar solvents in leaving the position of equilibrium in the condensed phase of ethyl

acetoacetate, namely 7.4% of enol¹³, practically unaltered. This, however, is to be expected in view of its dielectric constant value ($\epsilon_{25} = 20.797$) compared with that of ethyl acetoacetate ($\epsilon_{25} = 15.7$) so that there would be no appreciable change in dielectric constant resulting from dilution with acetone.

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