

**406.** *Keto-Enol Equilibria of Ethyl Acetoacetate in Solution.  
Dielectric Polarisation Indications.*

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The dielectric polarisations of equilibrated ethyl acetoacetate in a number of solvents have been measured at 25°. From the squares of the apparent moments so obtained the following enol-percentages at infinite dilution are calculated: in hexane, 63; in carbon tetrachloride, 25; in benzene, 25; in carbon disulphide, 43; in toluene, 39; in ether, 14; in chloroform, *ca.* 0. These figures are reconcilable with recorded analyses by Meyer's bromine-titration method. No correlations with specific properties of the media have been discovered.

THIS paper concerns the effects of media on the keto-enol equilibrium of ethyl acetoacetate, for which nearly all the recorded data have hitherto been obtained by the "bromine titration"

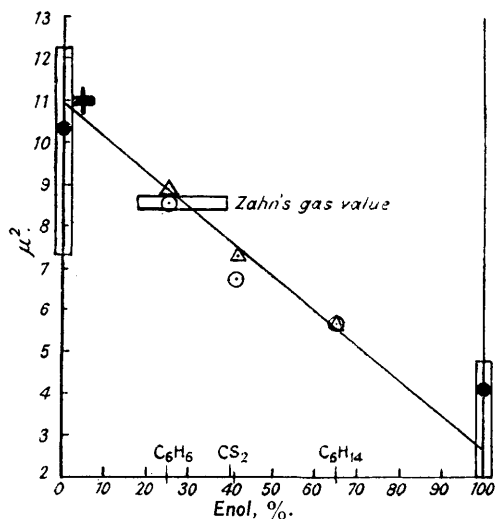
procedure of Meyer and his collaborators (*Annalen*, 1911, **380**, 226; *Ber.*, 1911, **44**, 2718; 1912, **45**, 2852; *Ber.*, 1920, **63**, 1410). Conant and Thompson (*J. Amer. Chem. Soc.*, 1932, **54**, 4039) later used Meyer's original form in estimating the free energy change of enolisation, notwithstanding criticisms and modifications of this technique previously made by Grossmann (*Z. physikal. Chem.*, 1924, **109**, 305) and Hantzsch and Krober (*ibid.*, 1930, **147**, 293). It is well known that consistency of numerical results can be obtained only by an exact adherence to a set manipulative routine. It seemed, therefore, that check analyses by different means might be useful. Physical methods (in which the tautomeric components are not subjected to reagents) are obviously preferable. To date—with the single exception of refractometry—these have not been accurately applied to solutions (see Beilstein, "Handbuch, Erste Ergänzungs-Werk," III, 223, for summary and references).

*Present Work.*—We have accordingly investigated the suitability of dielectric-polarisation measurements for this purpose. The apparent dipole moments of ethyl acetoacetate have been determined in seven solvents by routine methods (see Experimental section for details). Our values are listed in Table I :

TABLE I.

Solvent :	Hexane.	C <sub>6</sub> H <sub>6</sub> .	CS <sub>2</sub> .	CCl <sub>4</sub> .	PhMe.	CHCl <sub>3</sub> .	Et <sub>2</sub> O.
$\infty P_1$ (at 25°), c.c. ....	151	209	173	228	192	263	155
$\mu_{\text{apparent}}$ , D. ....	2.39	2.92	2.60	3.07	2.75	3.36	2.42

These data of course refer to the ester at "infinite dilution," a condition which enables the effects of different solvents to be expressed on an equivalent basis. Such results, however,



cannot immediately be compared with those by "bromine titration." Fortunately Meyer and Kappelmeier tabulate analyses in benzene, hexane, and carbon disulphide, over wide concentration ranges [at room temperature, it is true, but for the pure liquid "das Gleichgewicht verändert sich bis zum Siedepunkt kaum mit der Temperatur" (Beilstein, *loc. cit.*), whilst for solutions, the changes for a 5° interval are small—probably not more than 2% of the enol content (Meyer and Willson, *Ber.*, 1914, **47**, 832)]. We find that their figures plot smoothly against proportions of total solute in the solutions, and at  $w_1 = 0$  indicate an enol-% of 65 in *n*-hexane, 25 in benzene, and 41 in carbon disulphide. If it is accepted that at equilibrium our solutions can be regarded as containing only two forms, of unknown moments  $\mu_E$  and  $\mu_K$  respectively, then the squares of these moments should be related to  $\mu_{\text{apparent}}^2$  by a simple-mixture formula.

As a first check we explored this possibility by plotting observed  $\mu^2$  values against the enol-percentages quoted above (see figure, points ○). The three points suggest that a straight line relation may not be incorrect. The present measurements are almost certainly not free from "solvent" influences. By noting the moments found by Müller (*Physikal. Z.*, 1933, **34**, 5) for acetone in these solvents, and adjusting (by simple proportion) our observations to "gas" values (using the squares of the moments since it is the orientation polarisation, a function of  $\mu^2$ , which varies with the solvent) we obtained results lying nearer to a straight line (figure, points Δ compared with points ○).

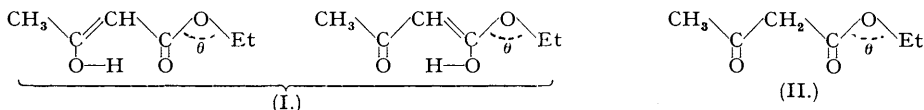
A further datum can be obtained from the liquid equilibrium ester, from which enol contents of from 2% (by refractive index measurements; Knorr, Rothe, and Averbeck, *Ber.*, 1911, **44**, 1147) to 7.4% (by bromine titration; Meyer, *loc. cit.*) are recorded. In another connection, Onsager (*J. Amer. Chem. Soc.*, 1936, **58**, 1486) has shown that the true orientation polarisation of a molecule should be expressible by terms including the dielectric constant, density, and refractive index, as measured for the *liquid* (and not the dissolved or gaseous) phase, by :

$${}_0P = \frac{(\epsilon - n^2)(2\epsilon + n^2)}{\epsilon(n^2 + 2)^2} \cdot \frac{M}{D}$$

whilst Böttcher (*Physica*, 1939, **6**, 59) has tested this calculation successfully for eighteen substances, including acetone and ethyl acetate. It may therefore apply to ethyl acetoacetate. We have accordingly made the necessary determinations at 25° (see Experimental section), and find  ${}_0P = 224.5$  c.c., from which a theoretical  $\mu_{\text{gas}}$  value (corresponding to 2—7% of enol) of 3.3 D. is obtained. The appropriate indication on the figure is +.

Only one direct measurement of the moment of vapourised ethyl acetoacetate is available (Zahn, *Physikal. Z.*, 1933, **34**, 570). Observations were made over the rather small temperature interval 394—431° K. The apparent moment lay between 2.91 and 2.95 D. (average quoted by Zahn, 2.93 D). The keto-enol proportions present under Zahn's conditions are unknown, but the reasonable guess may be made (bearing in mind the experimental procedure commonly adopted for estimating the dielectric constants of relatively high-boiling liquids) that the equilibrium approximated to that occurring in the vapour entering the condenser during a normal vacuum distillation. Knorr, Rothe, and Averbeck (*loc. cit.*) have examined such condensates, finding enol-percentages ranging from 18 to 39%. The area bounded by these extremes and  $\mu^2 = 8.47$ —8.70 is included on the figure.

*Numerical Values of  $\mu_E$  and  $\mu_K$ .*—The limits within which these are likely to fall can be estimated if (a) the configurations of both forms are such that the heavier component atoms in each are as nearly as possible in common positions, (b) the O . . . H . . . O bridge is rectilinear, between 2.4 and 2.8 Å. in length (Robertson, *Trans. Faraday Soc.*, 1940, **36**, 913), and has no resultant moment towards either oxygen atom, and (c) the carboxy-group retains throughout the "trans"-structure assigned to it by Marsden and Sutton (*J.*, 1936, 1383).



Accordingly we consider, as the major contributing forms, (I) and (II), where all carbon-intervalency angles are approximately 120°, whilst  $\theta$  (cf. Bennett, *Trans. Faraday Soc.*, 1934, **30**, 853; Hampson, Farmer, and Sutton, *Proc. Roy. Soc.*, 1933, **143**, A, 158) may vary from 60° (as in ethylene oxide,  $\mu_{\text{gas}} = 1.9$  D.) to 110—120° (as in diethyl ether,  $\mu_{\text{gas}} = 1.1$  D.; see *Trans. Faraday Soc.*, 1934, appendix, for all values of  $\mu$  quoted without reference).

The chief polar links will produce resultants, for (I), of  $1.0 + 2.3 - (1.1 \text{ to } 1.9) = 2.2$  to  $1.4$  D., and, for (II), of  $2 \times 2.3 - (1.1 \text{ to } 1.9) = 3.5$  to  $2.7$  D. (Eucken and Meyer's link moments, *Physikal. Z.*, 1929, **30**, 397, being used, and the fragment  $\text{Me}-\text{C} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{O}$  being taken as equivalent to a component of 1 D. acting along the C—O bond). These ranges are indicated on the two ordinates of the figure. Beyaert (*Natuurw. Tijdschr.*, 1937, **19**, 197) has recorded an attempt at direct measurement on the enolic form at  $-80^\circ$  in carbon disulphide solution. The moment found was 2.04 D. Using this figure and assuming that the ester was 16.8% enolised in benzene, he estimated  $\mu_{\text{keto}}$  from observations at room temperatures in this solvent as 3.22 D. (see figure, points ●). Beyaert notes that during solubility experiments at  $-80^\circ$  in carbon disulphide no correction was made for the small amount of the ketonic form present, and we therefore suspect that his value of  $\mu_{\text{enol}}$  is thereby too high, and, consequently, his  $\mu_{\text{keto}}$  too low. This is consistent with the figure (which suggests  $\mu_{\text{keto}}/\mu_{\text{enol}} = 3.3/1.7$ ).

*Relative Proportions at Equilibrium.*—From the figure the approximate proportions in each solvent at infinite dilution appear to be as in Table II.

TABLE II.

Solvent.*	% enol.	Enol/keto ratio.
Hexane .....	63	1.70
Carbon tetrachloride .....	25	0.33
Carbon disulphide .....	43	0.75
Benzene .....	25	0.33
Toluene .....	39	0.64
Ether .....	14	0.16

\* Listed in ascending order of  $\epsilon_{25}$ .

The case with chloroform as a solvent has not been included since it may be exceptional. It is known that chloroform-acetone mixtures show abnormalities in several physical properties, notably vapour pressure, viscosity, dielectric polarisation, and infra-red spectrum. For the third of these, Glasstone (*Trans. Faraday Soc.*, 1937, **33**, 200) found unexpectedly high values,

attributed to association of a co-operative type ( $R_2C \overset{\rightarrow}{=} O \overset{\rightarrow}{H} - CCl_3$ , where the arrows indicate the directions of the contributing moments, to which must be added induced moments acting in the same sense). As to the infra-red spectra, Gordy (*J. Chem. Physics*, 1939, **7**, 163) observed that neither of these two liquids alone had an absorption band near  $4\mu$ , which was however displayed prominently by mixtures. He interpreted this as evidence of an intermolecular H bond ( $Cl_3C-H-O=CMe_2$ ). Such suspicions are further justified by the work of Horiuti and Sakamoto (*Bull. Chem. Soc., Japan*, 1936, **11**, 627) which demonstrates (by the ready exchange between hydrogen and deuterium in heavy water) that the H of  $CHCl_3$  has a tendency to separate as a proton in certain circumstances.

Similar factors may operate with ethyl acetoacetate in chloroform. Meyer (*loc. cit.*) reports about 92% of the keto-form in such solutions. The qualitative indications of our measurements are likewise that the enol-percentage is extremely small.

*General Solvent Effects on Equilibrium.*—As a preliminary it is relevant to mention that recorded investigations (Beilstein, *op. cit.* for references) have shown ethyl acetoacetate to be unimolecular in solution.

Like many previous authors (Michæl and Hibbert, *Ber.*, 1908, **41**, 1080; Dimroth, *Annalen*, 1910, **377**, 127; Meyer, *ibid.*, 1911, **380**, 226) we have explored the possibility of a general quantitative correlation between enol:keto ratios and single properties of solvents. From Table II it is obvious that the numerical value, alone, of the dielectric constant (cf. *Annalen*, 1913, **399**, 91) is not immediately connected with either the enol-percentage or the enol/keto ratio. Some signs of parallelism have been found with expressions of the type:  $\text{Enol-\%} = 100 \cdot e^{-\mu_{\text{enol}}(\epsilon-1)/\mu_{\text{keto}}} = 100 \cdot e^{-1.7(\epsilon-1)/3.3}$ , *e.g.* :

	Solvent: Hexane.	CS <sub>2</sub> .	PhMe.	C <sub>6</sub> H <sub>6</sub> .	CCl <sub>4</sub> .	Et <sub>2</sub> O.
$\epsilon$ .....	1.89	2.63	2.37	2.27	2.23	4.27
Obs. Enol-% .....	63	43	39	25	25	14
Calc. ditto .....	63	44	49	52	53	19

Similar attempts, introducing other intuitively reasonable physical data, have not been more successful. Whenever  $\epsilon$  is involved, *trends* in accord with experiment are forecast, *e.g.*, that solvents with large dielectric constants should give low enol-percentages. The case when  $\epsilon = 1$  (*i.e.*, the gaseous state) should correspond to an enol-percentage of 100. This, on thermodynamic grounds, could never be wholly correct, but no protracted equilibrations in the vapour state are yet on record (the work of Zahn, and Conant *et al.* involved the near participation of the *liquid* phase).

Earlier discussions on reciprocal reactions (*e.g.*, by van't Hoff, "Lectures on Theoretical and Physical Chemistry," trans. Leffeldt, Arnold, 1898, **1**, 221) do not greatly assist the setting up of "models" for keto-enol-solvent systems. The "van't Hoff-Dimroth rule" has, of course, been found applicable to an assorted range of equilibria (Moelwyn-Hughes, "Kinetics of Reactions in Solution," 2nd Edn., Oxford Univ. Press, 1947, 188), but it utilises solubility data which themselves are of an experimental nature and not yet related to specific molecular quantities. We feel that the stabilisation of the keto-form through H-bonding with another molecule (*e.g.*,  $R \cdot O-H \cdots O=CMe \cdot CH_2 \cdot CO_2Et$ ), may be one important part of a qualitative explanation of solvent effects. To this we would add the extra stability which surrounding polar solvent molecules could confer on (II) by association with antiparallel alignment of dipole moments. Thus, solvents which readily form H-bonds with ketones or which possess high localised polarities (localised because certain mutual geometrical requirements are obvious) should show preferential development of the keto-form. That such a prediction is broadly in agreement with facts is seen, not only from our own results at infinite dilution, but also from those of Meyer *et al.* (*loc. cit.*, although these refer to various concentrations, and might be different at infinite dilution) :

Solvent:	H <sub>2</sub> O.	H-CO <sub>2</sub> H.	AcOH.	MeOH.	EtOH.	Pure ester.	COMe <sub>2</sub> .	PhNO <sub>2</sub>
Temperature, °C. ...	0	20	20	0	0	20	0	18
%-Enol .....	0.4	1.1	5.7	6.9	12.7	7.4	7.3	10.1

In neutral solvents of low polarity (*e.g.*, hydrocarbons, which do not normally engage in H-bonding) the ester is free to form its internal H-bridge. It evidently does this more easily than the related intermolecular process. Were this not so, the liquid equilibrium (pure ethyl acetoacetate) would be *ca.* 50:50 and not 7:93 as actually observed. Noting, however, that Badger and Bauer (*J. Chem. Physics*, 1936, **4**, 469, 71; 1937, **5**, 839) have found diacetone alcohol—whose structure should favour internal chelation—to have less than 0.75 of its molecules

chelated in carbon tetrachloride solution, we infer that the factors leading to an internal H-bond can sometimes only slightly outweigh those leading to an external one. In the condensed phase of ethyl acetoacetate, therefore, association by dipole-dipole forces may control the equilibrium; the fact that dissolution in acetone (similar  $\mu$  and  $\epsilon$  values) does not significantly alter the enol-%, further supports this.

We conclude, accordingly, that the predominant determinant of the keto-enol ratio lies with the keto- and not the enol-form. Of course, strongly basic (Brönsted sense) solvents might assist enolisation *via* intermolecular association (*e.g.*,  $C_5H_5N \cdots H-O-CMe=CH\cdot CO_2Et$ ) but experimental studies in such media are, at present, sparse.

#### EXPERIMENTAL.

*Materials.*—The solvents used were prepared for use as follows. Hexane, by shaking with sulphuric acid, washing, drying (Na), distillation, and storage over sodium wire; benzene, by drying "thiophen-free" material (Na wire), partly freezing, decanting, and storing the remelted portion over sodium wire; carbon tetrachloride, by boiling under reflux over mercury, shaking with sulphuric acid, dilute aqueous sodium hydroxide, and water successively, drying ( $CaCl_2$ ), fractionating, and storing over calcium chloride; carbon disulphide, by prolonged shaking of an "AnalaR" sample with mercury and calcium chloride, fractionating, and storing in dry air; chloroform, by shaking with aqueous sodium hydrogen sulphite, water, concentrated sulphuric acid, and water, followed by fractionating, and storing over calcium chloride; ether, by shaking with aqueous silver nitrate, dilute aqueous sodium hydroxide, and water, drying ( $CaCl_2$ , before Na wire), fractionating, and storing over sodium; toluene, by shaking with concentrated sulphuric acid, then dilute aqueous sodium hydroxide, then water, drying ( $CaCl_2$ , then Na), distilling, and storing over sodium wire.

Ethyl acetoacetate, as purchased (B.D.H.), was dried ( $CaCl_2$  or  $Na_2SO_4$ ), filtered, and distilled. Only the middle third, b. p.  $89^\circ/30$  mm. (cf.  $87.8^\circ/29.32$  mm., Beilstein, Handbuch, *loc. cit.*), was collected. Solutions were prepared by weight and set aside overnight at room temperature before any measurements were made; this precaution seemed desirable in view of the reports concerning time variance of the initial densities, viscosities, and magnetic susceptibilities of freshly distilled batches of ester (cf. Beilstein, *op. cit.*, p. 224). The measurements of Grossmann (*loc. cit.*) on the rates of enolisation of the keto-form, however, indicate that equilibrium is established in ordinary glass containers in less than 12 hours.

*Apparatus.*—Preliminary observations (by G. J. Rayner, made at University College, London, 1939), which are incorporated in Table I, were obtained with the resonance apparatus described in "Dipole Moments" (Methuen, London, 1938, p. 29). For the majority of the data, however, the simpler circuits mentioned recently (Calderbank and Le Fèvre, *J.*, 1948, 1949; *op. cit.*, 2nd Edn., 1948, Chapter II) have been utilised.

The pure ester was examined in a small (about 5-c.c. capacity) Pyrex cell, the plates of which were constructed from two 1.5-cm. lengths of brass tubing, spaced with glass beads, and supported by stout tungsten wires passing through the glass to mercury-containing side-arms. From the latter, connection was made directly to a co-axial union, mounted on the bridge holding the cell assembly in the thermostat, and from thence, *via* 2 feet of co-axial cable, to the oscillator chassis. The cell was filled and emptied by suction without removal.

Readings on the variable condenser were noted with air and a number of reference liquids filling the cell. Together with the solvents listed below, we have used purified ethylene dichloride and acetone, standard figures for which are available:

$C_2H_4Cl_2$ :	$\epsilon_{25^\circ} = 10.35_8$ (Davies, <i>Phil. Mag.</i> , 1936, <b>21</b> , 1008).
	$\epsilon_{25^\circ} = 10.36 \pm 0.02$ (Sugden, <i>J.</i> , 1933, 768).
$C_3H_8O$ :	$\epsilon_{25^\circ} = 19.11_5$ , from $\log \epsilon = 1.2914 - 0.00201 (t^\circ - 20^\circ)$ , Åkerlof ( <i>J. Amer. Chem. Soc.</i> , 1932, <b>54</b> , 4125).
	$\epsilon_{25^\circ} = 19.06$ (Le Fèvre, <i>Trans. Faraday Soc.</i> , 1938, <b>34</b> , 1127).

A mean value of (Reading plus liquid minus reading plus air)/ $(\epsilon - 1)$  was so obtained. Ethyl acetoacetate, which had stood for 2 days in a glass flask after distillation, was then drawn into the cell, etc., its dielectric constant at  $25^\circ$  being thus determined as 15.33 (average result of 5 experiments; Drude, *Z. physikal. Chem.*, 1897, **23**, 267, gives 15.7 at  $22^\circ$ ). For the application of Onsager's equation (see above) we have calculated  $n^2$  from  $[R_L]_D = 32.1$  and  $d^2 = 1.02z$  (Dunstan and Stubbs, *J.*, 1908, **93**, 1921).

*Solutions.*—Data for these are tabulated below under:  $w_1$ , the weight fractions of ester in the solutions;  $\epsilon$ , the dielectric constants of the latter; and  $d$ , their densities. Subscripts 1 and 2 refer to solute and solvent respectively. The quantity  $\alpha\epsilon_2$  represents  $(\epsilon_{12} - \epsilon_2)/w_1$ , which is required later (p. 1914).

The dielectric constants of all solutions are relative to the appropriate pure solvents, for which values have been taken, as follows:

Solvent :	$\epsilon_{25^\circ}$	Source.
Hexane .....	1.8938	Determined against benzene.
Benzene .....	2.2725	Hartshorne and Oliver, <i>Proc. Roy. Soc.</i> , 1929, <b>123</b> , 664.
Carbon disulphide .....	2.6349	Determined against benzene.
Carbon tetrachloride .....	2.2270	Le Fèvre, <i>loc. cit.</i>
Toluene .....	2.3666	Determined against benzene.
Chloroform .....	4.7240	Ball, <i>J.</i> , 1930, 570.
Ether .....	4.265	Le Fèvre, <i>loc. cit.</i>

<i>Hexane.</i>					
$100w_1$ .	$\epsilon_{12}^{25}$ .	$d_4^{25}$ .	$100w_1$ .	$\epsilon_{12}^{25}$ .	$d_4^{25}$ .
0	1.8938	0.65542	9.425	2.2820	0.67626
1.737	1.9554	0.65906	12.235	2.4223	0.68293
2.671	1.9874	0.66107	14.275	2.5335	0.68768
5.614	2.1107	0.66751	17.577	2.7319	0.69614
5.706	2.1124	0.66770	19.269	2.8411	0.70038
5.725	2.1195	3.66799	21.008	2.9594	0.70473
6.013	2.1303	0.66863			

<i>Benzene.</i>					
0	2.2725	0.87378	6.423	2.7585	0.88153
0.6216	2.3162	0.87457	7.101	2.8098	0.88236
1.229	2.3580	0.87529	7.843	2.8674	0.88354
1.732	2.3942	0.87587	9.140	2.9578	0.88533
1.9245	2.4060	0.87615	11.745	3.2070	0.88855
2.150	2.4308	0.87669	12.144	3.2419	0.88909
3.264	2.5072	0.87770	18.101	3.8102	0.89692
3.873	2.5480	0.87852	21.233	4.1294	0.90104
4.2575	2.5788	0.87867	24.827	4.5167	0.90593
4.604	2.6163	0.88001	31.157	5.2347	0.91470
4.632	2.6230	0.87937			

<i>Carbon disulphide.</i>					
0	2.6349	1.2585	6.914	3.2968	1.2324
0.8536	2.7045	1.2551	8.461	3.4600	1.2269
2.853	2.8927	1.2473	10.067	3.6386	1.2214
2.976	2.9023	2.2469	14.115	4.1134	1.2080
5.160	3.1171	1.2387			

<i>Carbon tetrachloride.</i>					
0	2.2270	1.5844	3.4168	2.6303	1.5544
1.0082	2.3612	—	4.4055	2.7008	1.5480
1.8346	2.4559	1.5687	5.1067	2.7871	1.5386
2.7389	2.5623	—	5.3960	2.8390	1.5356
3.0524	2.5983	1.5570	10.246	—	1.4899

<i>Toluene.</i>					
0	2.3666	0.86051	8.3270	2.9588	0.87058
1.1248	2.4392	0.86183	11.058	3.1043	0.88010
3.6517	2.6093	0.86452	15.922	3.6155	0.88024
4.1189	2.6288	0.86573	20.542	4.0048	0.88592
5.2530	2.7318	0.86663			

<i>Chloroform.</i>					
0	4.7240	1.4678	4.2566	5.9833	1.4405
2.3513	5.4318	1.4526	4.5524	6.0355	1.4387
3.0942	5.6523	1.4478	6.7401	6.5496	1.4255
3.2911	5.7080	1.4466	7.1733	6.6861	1.4230

<i>Ether.</i>					
0	4.265	0.70768	6.1221	4.679	0.72204
1.4401	4.348	0.71040	6.2188	4.691	0.72224
1.8484	4.378	0.71047	9.3786	4.910	0.72919
2.1948	4.405	0.71195	9.8144	4.940	0.73104
3.3755	4.474	0.71558	10.584	5.009	0.73343
5.7518	4.652	0.72180	11.135	5.050	0.73490

Inspection will reveal that in most cases  $\alpha\epsilon_2$  and  $\beta d_2$  are not invariant with  $w_1$ . Since the ratio keto/enol changes with concentration this is not unexpected. The dependence is, however, rectilinear. We have accordingly calculated  $\infty P_1$  (the total polarisation at infinite dilution) from the values of  $\alpha\epsilon_2$  and  $\beta d_2$  extrapolated to  $w_1 = 0$ , the equation,  $\infty P_1 = M_1[\rho_2(1 - \beta) + C\alpha\epsilon_2]$ , being used (cf. *J.*, 1937, 1805). The molecular refraction is taken as 33 c.c. from several data recorded in the literature (cf. Beilstein, *op. cit.*).

*Calculations of apparent moments, etc.*

Solvent.	$(\alpha\epsilon_2)_{w_1=0}$ .	$(\beta d_2)_{w_1=0}$ .	$c$ .	$\rho_2$ .	$\infty P_1$ .	$\mu_{app.}$ D.
Hexane .....	3.40	0.207	0.3019	0.3502	151	2.3 <sub>9</sub>
Ether .....	5.06	0.090	0.1080	0.7364	155	2.4 <sub>2</sub>
Carbon disulphide .....	8.67	0.398	0.1180	0.2803	173	2.6 <sub>0</sub>
Toluene .....	6.36	0.115	0.1828	0.3637	192	2.7 <sub>5</sub>
Benzene .....	7.00	0.121	0.1881	0.3409	209	2.9 <sub>2</sub>
Carbon tetrachloride .....	13.90	-0.853	0.1060	0.1832	228	3.0 <sub>7</sub>
Chloroform .....	32.65	-0.665	0.4521	0.3773	263	3.3 <sub>6</sub>

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