

solutions, rather than upon a difference in the solubility of the non-enantiomorphic salts.

The resolution of an asymmetrically substituted amine, benzylethylaniline, possessing no carbon asymmetry, was finally attempted employing, in turn, 1-bromo-*d*-camphor-10-sulfonic acid, and *d*-camphor-1'-sulfonic acid. No evidence of resolution was found.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE FREE ENERGY OF ENOLIZATION IN THE GASEOUS PHASE OF SUBSTITUTED ACETOACETIC ESTERS

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RECEIVED JUNE 1, 1932

PUBLISHED OCTOBER 5, 1932

Previous measurements of the equilibrium constants of the change keto \rightarrow enol have all been carried out with solutions of the two components or with the equilibrium liquid mixture. K. H. Meyer,¹ the first investigator to obtain satisfactory quantitative results, found that the nature of the solvent affected enormously the equilibrium constant. It was thus difficult to obtain a satisfactory comparison of a series of substituted ketonic esters or diketones; his proposal to compare them all in the same solvent was only partially successful as the comparisons in many cases varied with the nature of the solvent. The use of the pure liquid equilibrium mixtures as a basis of comparison is clearly open to the same sort of error and a serious and unknown solvent effect is introduced into the measurements. It seemed probable that the greatest regularity between structure and free energy of enolization would be found by taking the gaseous phase (preferably at low pressure) as the standard state. Such a choice of the standard state in the reduction of a series of chloroquinones brings out regularities which are obscured by physical forces when the solid state or a solution is used as the standard state.² We have therefore undertaken to measure the equilibrium constant of enolization in the gaseous state for acetoacetic ester, eight substituted acetoacetic esters, four β -diketones and a few other related compounds. The results show clearly that there is a regularity between the structure of the compound and the free energy of enolization in the gaseous state.

Since the interconversion of the two tautomeric isomers does not proceed at all readily in the gaseous state at room temperature, it was necessary to use the liquid phase as an intermediary. It is clear that if chemical

¹ Meyer, *Ber.*, **45**, 2846 (1912).

² Conant, *THIS JOURNAL*, **49**, 293 (1927); a further discussion of this point and a preliminary statement of the results of the present investigation are given in *Ind. Eng. Chem.*, **24**, 466 (1932).

equilibrium involving two isomers is maintained in a liquid throughout an experiment and if the liquid in turn is in physical equilibrium with the gas, the composition of the vapor must represent the equilibrium condition in the gaseous state. If condensation of the vapor now takes place without isomerization, the composition of the condensate is a correct measure of the equilibrium corresponding to the gaseous state. The experimental procedure was briefly as follows. The pure liquid compound (a mixture of the two forms) was placed in a Pyrex flask of 50-cc. capacity and a small amount of solid anhydrous barium hydroxide was added as a catalyst. The flask was sealed to a Pyrex receiver immersed in an ether-carbon dioxide bath and evacuated with a pump to a pressure of less than 0.01 mm. of mercury. Physical equilibrium between the liquid and gaseous phases was assured by rocking the flask back and forth mechanically so that the surface was continuously renewed by the agitation. To prevent refluxing the neck of the vessel and connecting tube were warmed by an electric heating coil wound on the apparatus. The temperature of the liquid in the flask was controlled by placing the flask in a small water-bath whose temperature was read throughout the distillation.

A great many experiments were carried out to test the assumptions underlying this method. The Pyrex receiver, which consisted of a tube about 1 cm. in diameter and 10 cm. long, was rendered non-catalytic by the method of Rice and Sullivan.³ This consists of heating the carefully cleaned tube to the point of collapse in a blast lamp; the Pyrex test-tube into which the distillate was poured and the Pyrex pipet used for transferring a sample for analysis received the same treatment. As a proof of the non-catalytic effect of the receiver, the fact may be cited that 77% enolic acetoacetic ester in such a receiver dropped to 45% only after fifteen hours at room temperature (equilibrium concentration 7%). Since the receiver was at about -80° throughout a determination and the contents were analyzed within five minutes after the receiver had been warmed to room temperature, it is evident that any isomerization in the receiver was negligible. A further test of the point at issue was afforded by the results of successive sampling of the contents of the receiver. In every case except two the results obtained were consistent. In the case of acetylacetone and methyl acetoacetate, however, the pouring from the receiver to the "aseptic" test-tube had to be omitted. With these compounds the receiver was cut off from the apparatus and the material rapidly withdrawn from the cold receiver with an aseptic pipet. Under these conditions successive samples gave results which showed but a slight decrease of enol content within the time required for analysis.

Both the direct and indirect bromine titration procedures were tried as methods of determining the enol content of the distillate. With un-

³ Rice and Sullivan, *THIS JOURNAL*, 50, 3048 (1928).

substituted acetoacetic ester and acetylacetone, the indirect method (using beta naphthol, potassium iodide and titrating the iodine evolved) gave slightly higher results than the direct method. With all the other compounds, the direct method when properly carried out was found much more reliable;⁴ the difficulty with the indirect method when applied to the substituted acetoacetic esters is that the iodo compound liberates its iodine but slowly and the apparent enol content, therefore, depends on the time of heating of the solution, reaching as a limit a value near that obtained by the direct method. Since we were always working with mixtures richer in enol than the equilibrium mixture, any error caused by the catalytic effect of the added bromine would tend to cause our results to be too low. Actually, however, they were somewhat higher than the limit approached by the indirect method. For this reason, and because of the consistency and reproducibility of the results obtained by the direct titration, we employed it in every case except those mentioned above. The procedure was as follows. The sample was introduced from a calibrated "aseptic" pipet into 20 cc. of ethyl alcohol cooled to -10° . The solution was immediately titrated with approximately 0.1 *N* bromine in methyl alcohol until a yellow color was permanent for several seconds; the titration takes less than a minute. Immediately a volume of the bromine solution of exactly the amount used in the titration is run into another flask, an aqueous solution of potassium iodide added and the mixture titrated with standard thiosulfate solution in the usual manner; the amount of bromine consumed by the sample is calculated from the thiosulfate used.

The assumptions in regard to the attainment of chemical and physical equilibrium during the distillation can be tested by stopping the distillation from time to time and analyzing the distillate. Unless equilibrium conditions prevail, successive distillates would hardly be expected to have the same composition. This is easily shown by omitting the catalyst from the liquid phase, when the first distillate is high in enol and progressively diminishes in enol content with each fraction. Typical results which were obtained under what we believe to have been equilibrium conditions, were as follows: acetoacetic ester, four successive fractions had the following enol content: 45.6, 46.3, 47.9, 47.9%; three successive fractions of α -propyl ethylacetoacetate had the following compositions: 11.9, 12.2, 12.2% enol. In two cases we had clear evidence that we were not dealing with equilibrium conditions; one of these was with α -*sec.*-butyl ethyl acetoacetate using the usual barium hydroxide as a catalyst. The enol content of the fractions regularly diminished from 16.5 to about 8%. That the failure was due to insufficient catalytic effect was shown by treating high enol *sec.*-butylacetoacetic ester (10.6%) with barium hy-

⁴ Dieckmann, *Ber.*, 55, 2470 (1922), gives a detailed discussion of the two methods.

dioxide in Pyrex, it required one hundred and sixty-eight hours for the liquid equilibrium state (8.8%) to be reached. By using a drop of tetramethylammonium hydroxide (a solution concentrated to a sirup on the water-bath) as a catalyst, fairly satisfactory results were obtained with the *sec.*-butyl compound. In the case of tricarbethoxymethane, no conditions were found that yielded a satisfactory equilibrium. Only a rough estimate of the value in the vapor phase could be obtained from an analysis of the very first distillate. The fact that these difficulties manifested themselves so clearly leads us to believe that equilibrium conditions were at hand in all the other cases where consistent results were obtained on the analysis of successive distillates. It should be further mentioned that it was found that the temperature of the neck of the distilling flask was of no influence provided it was sufficient to prevent refluxing and that the rate of distillation was without significance. The usual rate of distillation was about 20 cc. an hour.

The compounds used in this work were all carefully purified by a final fractional distillation under diminished pressure and were used shortly after preparation. Many of them are not stable and after several months' standing had sufficiently decomposed to give unreliable results. The purity of these compounds cannot be checked by means of the usual physical constants since the liquid phase is a mixture of isomers. An analysis of the carbon and hydrogen content, however, is a satisfactory method of detecting any considerable amount of impurity. This is particularly important in the case of the alkyl derivatives made by alkylation which might contain the unalkylated parent compound. Table I lists the compounds we employed, their source, our analytical data, and the enol content of the equilibrium liquid; the previous determination of the enol content of the pure liquid is given in the next to the last column.

Discussion of the Results

The results obtained are summarized in Table II. The first two columns of figures record the results obtained by the method just outlined, the per cent. of enol being the composition of the distillate under equilibrium conditions, the liquid being kept at 25°. The value of $\Delta F (= -RT \ln K)$ for the reaction keto (gas) \longrightarrow enol (gas) is given in kilogram calories per mole in the second column. The corresponding values of the percentage of enol and ΔF for the reaction in the liquid equilibrium mixture, in a 0.1 *M* hexane solution and a 0.1 *M* solution in absolute alcohol are given in the other columns. The solutions were allowed to stand till the increase of enol content reached a maximum; this usually required one day. In the case of α -ethylacetoacetic ester, the equilibrium was approached from both sides in hexane solution and in a number of cases piperidine was added to the solution (concn. 0.05 *M*) in a separate experi-

TABLE I
SUMMARY OF DATA ON PREPARATION AND PURITY OF COMPOUNDS

Substance	Preparation references	Analyses, %								Percentage enol in liquid		
		Carbon		Hydrogen				Previously determined				
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Found	Previously determined			
CH ₃ COCH ₂ COOC ₂ H ₅	Eastman product	55.4	55.23	55.31	55.28	7.70	7.79	7.83	7.77	7.3	7.4	<i>Ber.</i> , 44, 2718 (1911)
CH ₃ COCH(CH ₃)COOC ₂ H ₅	"Organic Syntheses," Vol. VII, p. 36	58.33		58.30	58.31	8.32		8.37	8.35	4.1	4.1	THIS JOURNAL, 52, 4358 (1930)
CH ₃ COCH(C ₂ H ₅)COOC ₂ H ₅	"Organic Syntheses," Vol. VII, p. 36	60.80		60.60	60.71	8.86		8.88	8.90	2.95	3.0	<i>ibid.</i> , 52, 4358 (1930)
CH ₃ COCH(C ₆ H _{7-n})COOC ₂ H ₅	"Organic Syntheses," Vol. VII, p. 36	62.75		62.45	62.58	9.30		9.35	9.30	7.0		
CH ₃ COCH(C ₆ H _{7-iso})COOC ₂ H ₅	Bischoff, <i>Ber.</i> , 28, 2620 (1895)	62.75		62.77	62.64	9.30		9.36	9.32	4.9		
CH ₃ COCH(C ₆ H _{9-n})COOC ₂ H ₅	"Organic Syntheses," Vol. VII, p. 36	64.5		64.42	64.36	9.68		9.36	9.44	6.1		
CH ₃ COCH(C ₆ H _{9-sec})COOC ₂ H ₅	THIS JOURNAL, 30, 1149 (1908)	64.5		64.7	64.9	9.68		9.62	9.55	8.4		
CH ₃ COCH(C ₆ H ₅)COOC ₂ H ₅	Beckh, <i>Ber.</i> , 31, 3160 (1898); Dimroth, <i>ibid.</i> , 36, 2243 (1903); Post, THIS JOURNAL, 52, 4358 (1930)	69.9		70.1	70.3	6.80		7.00	7.09	30.5	39.2	<i>ibid.</i> , 53, 1496 (1931)
											30.0	<i>ibid.</i> , 54, 1963 (1932)
CH ₃ COCH(CH ₂ C ₆ H ₅)COOC ₂ H ₅	"Organic Syntheses," Vol. VII, p. 36	70.9		71.3	71.0	7.27		7.31	7.27	4.9	4.9	<i>Ber.</i> , 45, 2854 (1912)
CH ₃ COCH ₂ COCH ₃	Kahlbaum preparation used	B. p. 137.5-139°						B. p. 137.5-138.5°		76.5	76	<i>ibid.</i> , 45, 2857 (1912)
										82	82	<i>Ann.</i> , 426, 161 (1922)
CH ₃ COCH(CH ₃)COCH ₃	THIS JOURNAL, 52, 3212 (1930); <i>J. Soc. Chem. Ind.</i> , 44, 462 (1925)	63.2		63.3	63.4	8.77		8.95	8.84	29.5	31.2	<i>Ber.</i> , 45, 2859 (1912)
											31.0	<i>Ann.</i> , 426, 161 (1922)
CH ₃ COCH(C ₂ H ₅)COCH ₃	THIS JOURNAL, 52, 3212 (1930); <i>J. Soc. Chem. Ind.</i> , 44, 462 (1925)	65.6		65.3	65.3	9.38		9.28	9.44	26.4	31	<i>ibid.</i> , 426, 161 (1922)
CH ₃ COCH(CH ₂ C ₆ H ₅)COCH ₃	THIS JOURNAL, 52, 3212 (1930); <i>J. Chem. Soc.</i> , 127, 797 (1925)	75.8		75.45	75.65	7.37		7.48	7.67	61		
CH ₃ COCH(COOC ₂ H ₅) ₂	<i>Ann.</i> , 266, 110 (1891); <i>Am. Chem. J.</i> , 14, 495 (1892); <i>Ann.</i> , 426, 161 (1922)	53.5		51.8	51.9	6.93		6.81	6.86	66.5	64	<i>Ber.</i> , 45, 2854 (1912)
										70	70	<i>Ann.</i> , 426, 161 (1922)
CH(CO ₂ CH ₃) ₃		M. p. 45-46°.						M. p. 43°; B. p. 111°-112° (4 mm.)		1.16		
CH(CO ₂ C ₂ H ₅) ₃	<i>Am. Chem. J.</i> , 14, 495 (1892)	51.7		51.6	51.5	6.90		6.75	7.09	0.7	0.2	<i>Ber.</i> , 45, 2864 (1912)
CH ₃ COCH ₂ COOCH ₃	<i>Ann.</i> , 257, 355 (1890)	51.7		51.65	51.95	6.90		7.14	7.28	5.7	4.9	<i>ibid.</i> , 45, 2869 (1912)

TABLE II

A TABLE OF THE FREE ENERGY CHANGE OF ENOLIZATION, EXPRESSED IN LARGE CALORIES, OF THE COMPOUNDS STUDIED. THESE ARE REFERRED TO FOUR DIFFERENT STANDARD STATES AT 25°

Substance	Gaseous phase		Pure liquid		0.1 M solution in hexane		0.1 M solution in abs. alcohol	
	% enol	ΔF	% enol	ΔF	% enol	ΔF	% enol	ΔF
CH ₃ COCH ₂ COOCH ₃	53.7-55.0	-0.1	5.7-6.0	1.6				
CH ₃ COCH ₂ COOC ₂ H ₅	45.3-46.9	0.1	7.3-7.8	1.5	48-50	0.0	9-11.0	1.2
CH ₃ COCH(CH ₃)COOC ₂ H ₅	13.5-14.5	1.1	4.0-4.2	1.9	10.3-12.9	1.1	5.1	1.7
CH ₃ COCH(C ₂ H ₅)COOC ₂ H ₅	9.8-10.2	1.3	2.9-3.1	2.1	14.0-15.0	1.1	3.0-4.0	2.0
CH ₃ COCH(C ₃ H _{7-n})-COOC ₂ H ₅	13.1-13.4	1.1	6.8-7.2	1.5	14.3-14.5	1.1		
CH ₃ COCH(C ₃ H _{7-iso})-COOC ₂ H ₅	6.0- 6.25	1.6	4.8-5.0	1.8	5.85-6.1	1.6		
CH ₃ COCH(C ₄ H _{9-n})-COOC ₂ H ₅	13.0-15.0	1.1	6.0-6.2	1.6	9.0-11.	1.3	5.7-6.4	1.6
CH ₃ COCH(C ₄ H _{9-sec.})-COOC ₂ H ₅	*8.0-10.0	*1.4	8.3-8.5	1.4	8.6-9.9	1.3	9.0-9.5	1.4
	^a (54.0-56.0)	^a (-0.15)						
CH ₃ COCH(C ₆ H ₅)COOC ₂ H ₅	*78-82	*-0.8	29.5-31.5	0.5	66-68	-0.4	30.4-31.0	0.5
	^a (9.0-10.0)	^a (1.6)						
CH ₃ COCH(CH ₂ C ₆ H ₅)COOC ₂ H ₅	11.0-14.0	1.2	4.8-5.0	1.8	11-13	1.2	5.0-5.5	1.7
CH ₃ COCH ₂ COCH ₃	91-93	-1.3	76-80	-0.7	91.4-92	-1.3	82.5-83.5	-1.0
CH ₃ COCH(CH ₃)COCH ₃	43.5-44.5	0.1	30-31	0.5	58.5-59.4	-0.2	30.6-32.3	0.4
CH ₃ COCH(C ₂ H ₅)COCH ₃	*34.0-37.0	*0.3	26-27	.6	26.2-26.7	0.6	27.0-30.4	.5
	^a (58.0-60.0)	^a (-0.25)						
CH ₃ COCH(CH ₂ C ₆ H ₅)COCH ₃	68.0-72.0	-0.5	61-62	-0.25	66-70.0	(-0.4-0.6)	45.0-47.5	-0.1
CH(COOCH ₃) ₂	8-16	1.0-1.4	1-1.2	2.6				

^a The three groups of results marked with an asterisk are of a lower order of accuracy since they are extrapolated from higher temperatures. The values in parentheses are those actually determined at 95°.

ment and the solution allowed to stand for twelve hours to ensure equilibrium. The probable accuracy of the method is indicated by giving the range of the analytical figures for the percentage of enol; the average has been taken as the most probable. The free energy values are significant we believe in most cases to within a tenth of a kilogram calorie. The values for phenyl- and benzylacetoacetic ester and benzylacetylacetone are subject to the uncertainty of an extrapolation from a higher temperature since the compounds were not sufficiently volatile at 25°. In all cases no experiment was accepted unless at least two successive fractions gave the same value of the enol content, and several separate experiments with fresh samples of material gave consistent results. In most cases more than one piece of apparatus was employed and in a few instances the results were duplicated several months later with a freshly prepared sample of ester.

A study of the data presented in Table II reveals that there is great regularity in the values of ΔF referred to the gaseous phase but this regularity disappears when the liquid equilibrium mixture or a solution is used as a basis of comparison. This is very clearly brought out in the summary of the effect of substitution on the values of ΔF referred to the different standard states given in Table III. It is evident that the liquid

TABLE III

Groups involved	ΔF (gas)	ΔF (liq.)	ΔF (Hexane)	ΔF (C ₂ H ₅ OH)
1. Replacement of H by primary alkyl group				
(a) In acetoacetic ester series				
CH ₃	1.0	0.4	1.1	0.5
C ₂ H ₅	1.2	.6	1.3	.8
C ₃ H ₇	1.0	.0	1.0	
C ₄ H ₉	1.0	.1	1.3	.4
CH ₂ C ₆ H ₅	1.1	.3	1.2	.5
(b) In acetylacetone series				
CH ₃	1.4	1.2	1.1	1.4
C ₂ H ₅	1.6	1.3	1.9	1.5
CH ₂ C ₆ H ₅	0.8	0.45	0.7-0.9	0.9
2. Replacement of H by secondary alkyl				
In acetoacetic ester series				
(sec.)-C ₃ H ₇	1.5	0.3	1.6	
(sec.)-C ₄ H ₉	1.3	-0.1	1.3	0.2
3. Replacement of carboxy by acetyl in compound ACOOC ₂ H ₅ where A is:				
CH ₃ COCH ₂ -	-1.4	-2.2	-1.3	-2.4
CH ₃ COCH(CH ₃)-	-1.0	-1.4	-1.3	-1.2
CH ₃ COCH(C ₂ H ₅)-	-1.0	-1.5	-0.7	
CH ₃ COCH(CH ₂ C ₆ H ₅)-	-1.7	-2.0		
4. Replacement of H by phenyl in acetoacetic ester				
C ₆ H ₅	-0.7	-1.1	-0.4	-0.7
Average deviation from ΔF (gas)	...	0.64	0.17	0.48

phase results are the most irregular and the values obtained with dilute alcoholic solutions are nearly as bad. On the other hand, a dilute hexane solution seems to approximate the gaseous state in most instances. The regularity with this solvent is, however, less than with the gaseous phase, and one could not be certain that with other compounds the errors might not be larger. For ketonic esters and diketones, the use of a dilute hexane solution will probably yield results significant to ± 0.3 kg. cal. It is clearly useless to make measurements with the liquid equilibrium mixture if one is interested in energy differences less than 1.5 kg. cal. (a power of ten in the equilibrium constant).

The relation between structure and $\Delta F(\text{gas})$ shown by the data in Tables II and III needs but little discussion. The difference between the ethyl and methyl esters of acetoacetic ester is negligible (0.2) as would be expected. The primary alkyl groups are practically equivalent and only slightly more effective in decreasing enolization in the diketones than in the ketonic esters. The *sec.*-alkyl group is appreciably more effective in decreasing enolization than a primary group. The benzyl group is very like an alkyl group in its effect, but the phenyl group has a marked action in the opposite direction decreasing ΔF by 0.7 (increasing enolization). The acetyl group is more effective in increasing enolization than the carbethoxy by about one large calorie in a number of compounds. A few measurements with acetylmalonic ester (ethyl) and tricarbethoxymethane were not satisfactory and are not included in Table II but they indicated values of $\Delta F(\text{gas})$ of about -0.5 and 1.8 , respectively. Malonic ester showed no definite enol content in the distillate and $\Delta F(\text{gas})$ is therefore greater than $+6$ since 0.006% of enol could have been determined. A comparison of malonic ester and acetylacetone ($\Delta F \text{ gas} = -1.3$) shows that the replacement of two carbethoxy groups by two acetyl groups decreases ΔF by at least 7 Cal., or 3.5 Cal. per group. This is much larger than the effect summarized in Table III (3), where a similar replacement decreases ΔF by about 1-2 Cal. A comparison of acetylmalonic ester and tricarbethoxymethane shows a similar large effect of 2.8 Cal. caused by the change of one ester group to a methyl ketonic group. Even these approximate results are sufficient to show that no simple additive relation holds in regard to the effect of groups on ΔF of enolization. This is not strange considering that the enol form must have some such structure as that of a chelate ring,⁵ and that all the groups attached to the ring may exert a mutually dependent influence. (In every case which we have investigated the enol form is the more volatile which would certainly not be the case if the simple formula $\text{RC}=\underset{\text{OH}}{\text{C}}\text{COR}'$ were correct.)

⁵ N. V. Sidgwick, *J. Chem. Soc.*, 127, 907 (1925).

A number of experiments were performed keeping the temperature of the liquid in the distilling flask at different temperatures. The effect of change of temperature on the composition of the distillate is very slight and it was found impossible, therefore, to obtain significant values of the temperature coefficient of $K(\text{gas})$ and hence of $\Delta H(\text{gas})$. Errors which are negligible in determining ΔF are enormously magnified in determining ΔH by this method when it is small and only a short range of temperature is available. There is every reason to believe that the entropy change in the reaction keto (gas) \rightarrow enol (gas) is very small although one isomer is a chelate ring compound and the other an open-chain ketone or ketonic ester. We should expect that $\Delta H(\text{gas})$ would be very close to $\Delta F(\text{gas})$, therefore. In every case that we examined, except ethylacetylacetone, there was a definite decrease of $K(\text{gas})$ with increase of temperature; with ethylacetylacetone there was no appreciable change. The values of $\Delta H(\text{gas})$ varied from -2.3 to 0 , which, combined with the values of $\Delta F(\text{gas})$ for the appropriate compound, gave values for $T\Delta S$ ($298^\circ\text{K}.$) of from -0.3 to -2.7 , with many values near the latter figure. These indicate a much larger entropy change in the reaction than seems reasonable but in view of the uncertainties of the determination we are not inclined to attach much significance to this finding. Unfortunately, there seems no way of refining the method to yield significant information on this point.

The uncertainty in the temperature coefficient of $K(\text{gas})$ is reflected to a less extent in the extrapolation to 25° of the values obtained at 95° for the phenyl and benzyl compounds; they render the values for these compounds, however, much less certain than the others given in Table II. Possibly the irregularity between the effects of the benzyl group in the acetoacetic ester series and the acetylacetone series is due to experimental error caused by the uncertainties of the extrapolation (see Table III, where the benzyl group has the same effect as the alkyl groups in the acetoacetic ester series, but 0.8 kg. cal. less than the methyl or ethyl group in the acetylacetone series).

Summary

The free energy of enolization in the gaseous phase of a series of substituted acetoacetic esters and certain related compounds has been measured. A comparison of these results with the free energy change referred to the liquid equilibrium mixture or a dilute solution shows that regularities between structure and free energy are often obscured by solvent effects which may be as large as 1 kilogram calorie.