iodide in a number of solvents have been determined. The relative values of the constants are as follows: benzene, 1; nitrobenzene, 25; acetone, 12.8; methyl alcohol, 2.5; ethyl alcohol, 1.4; *n*-propyl alcohol, 1.11; *n*-butyl alcohol, 1.11; *iso*propyl alcohol, 1.07; *sec.*-butyl alcohol, 1.00 and *tert.*-butyl alcohol, 0.93.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

CATALYTIC STUDIES ON ACETOACETIC ESTER[1,2]

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Ethyl acetoacetate was discovered in 1863 by Geuther[3] and since then has been the subject of research by numerous workers. One phase of this work has comprised the identification of the two forms, their preparation in the pure condition, the equilibrium ratio of the liquid and of solutions in various media, and, in a semi-quantitative way, the rate of change of one form into the other. The purpose of the present work was to make a quantitative research on the rate of attaining equilibrium of the ester when rigorously purified according to the best technique available, and also when definite amounts of known catalysts were present. In our experiments we used Martin's method of distillation without ebullition:[4] by keeping a high vacuum (10^{-5} mm.) in our apparatus, we had no difficulty in distilling the ester at room temperature; in this way no bumping occurred and there was slight, if any, decomposition. Before allowing air to enter the apparatus, it was first bubbled through sulfuric acid to remove traces of aminic impurities and water, and then filtered to remove dust particles and sulfuric acid mist. Various kinds of containers were used, Pyrex, quartz and soft glass, either etched by corrosive cleaning agents, or with their inner surfaces smoothed by heating almost to the point of collapse. Using this special technique, we found that we could prepare samples of the ester of high enol content, which had a stability far greater than heretofore obtained. Our best samples had a half life of about 500 hours, as compared with rates less than one-tenth of this value reported by previous workers. There are no indications that we have reached the limit of stability, since the lowest rates appear to be due, at least in part, to traces of catalytic impurities still remaining.

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[1] In memory of Ira Remsen.

[2] Taken from a thesis submitted by Joseph J. Sullivan to the Graduate Faculty of the Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Geuther, *Jahr. der Chem.*, **1863**, 325.

[4] Martin, *J. Phys. Chem.*, **24**, 478 (1920).

Historical

As late as 1905, Brühl[5] considered the pure form of acetoacetic ester to be the keto form, although Wislicenus[6] had earlier proved that the two forms existed in dynamic equilibrium. Perhaps the most important point in this connection lies in devising an exact method of estimating the ratio keto/enol in samples of the esters. Methods involving some physical property or other[6] have been proposed, especially refractive index, which has been used by Knorr[7] and also by Meyer.[8] Of the chemical methods three may be mentioned. The first makes use of the formation of a purple enolate with ferric chloride,[9] and is really a colorimetric method. In the second method the enol form is titrated with a standard bromine solution, using ferric chloride, if desired, as indicator.[10] The third method is that perfected by Meyer and his collaborators[11] and takes place in the following steps: the ester, dissolved in alcohol, is treated with a slight excess of an alcoholic bromine solution, and the excess bromine is immediately removed by β-naphthol. The bromine adds quantitatively to the double bond of the enol, which then splits off hydrobromic acid giving the bromoketone. This is estimated by adding potassium iodide, warming slightly and titrating the liberated iodine by thiosulfate.

The analytical difficulties cleared, the next step was the preparation of the pure isomers. It had long been known that the freshly distilled ester contains from 20–25% enol,[12] and Meyer and his collaborators,[8,13] using a method of successive distillations *in vacuo*, finally obtained an ester of 99.8% enol. The last distillations were performed in a quartz apparatus, in which they found that only slight isomerization occurred. Other methods of preparing the pure isomers are extraction of the keto form with hexane,[14] and freezing out the keto form at $-78°$ as employed by Knorr.[6]

But little quantitative work has been done on the rate of rearrangement. A sample of freshly distilled ester, at 15°, followed by Meyer[10] for forty hours, shows on calculation a half life of 24.2 hours. In dissociating solvents, such as alcohol, the rate increases about 100 times, but the rate in these solvents is not much affected by halogen acids. In non-polar sol-

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[5] Brühl and Schröder, *Z. physik. Chem.*, **50**, 1 (1905).

[6] Wislicenus, *Ahrens Sammlung*, **2**, 230 (1898).

[7] Knorr and co-workers, *Ber.*, **44**, 1138 (1911).

[8] Meyer and Schoeller, *Ber.*, **53**, 1410 (1920).

[9] Knorr, *Ber.*, **44**, 2772 (1911); Meyer, *Ber.*, **45**, 2843 (1912).

[10] Meyer, *Ann.*, **380**, 212 (1911).

[11] Meyer and Kappelmeier, *Ber.*, **44**, 2718 (1911); *Ber.*, **45**, 2852 (1912); Finkelstein, *Ber.*, **43**, 1528 (1910).

[12] (a) Schaum, *Ber.*, **31**, 1964 (1898); (b) Traube, *Ber.*, **29**, 1720 (1896); (c) Hantzsch, *Ber.*, **43**, 3049 (1910).

[13] Meyer and Hopff, *Ber.*, **54**, 579 (1921).

[14] Meyer, *Ann.*, **380**, 231 (1911); Dimroth, *Ann.*, **377**, 127 (1910).

vents the rate is practically the same as for the pure liquid, but traces of halogen acids increase the rate enormously in these solvents. Meyer and Schoeller[8] give one specimen of work showing absence of isomerization in the vapor phase. In Table I we have collected the results of previous workers. For ease of comparison we have calculated the rate of change of enol ⟶ keto according to the method given later in the paper. The half life is the time in hours taken by the pure enol to fall to 50%. In the first three cases we have assumed the initial enol content to be 25%.

TABLE I

PREVIOUS WORK ON RATE OF ISOMERIZATION

Observer	Change in enol	Hours obs.	k_1	Half life, hours	Remarks
Traube[12b]	1.0244–1.0247	24	0.170	4.2	Density
Schaum[12a]	1.0278–1.0287	6	0.685	1.1	Density
D. and M.[15]	1.0209–1.0213	0.5	2.1	0.35	Viscosity
Meyer[10]	18.5%–7.9%	40	0.032	24	In quartz
M. and S.[8]	0%– 3%	20	.023	32	In quartz
Rumeau[16]	43%–33%	2	.15	5	In quartz
	52%–33%	4	.13	6	In quartz
	83%–58%	28	.013	58	In Pyrex
	52%–52%	4	...		In Pyrex
	52%–50%	4	.011	74	In Jena
	83%–10%	0.5	6.5	0.12	Soft glass

Quantitative investigation on the catalytic effect of impurities on the rate of rearrangement is also meager. Meyer and Willson[17] use oxalic acid (a trace) and Meyer and Hopff[13] phthalic anhydride (a few mg.) to stabilize a mixture of the isomers against aminic impurities, but give no measurements showing a relative improvement of conditions by their use. Hydrochloric acid and hydrobromic acid catalyze enolization, especially in non-polar solvents;[10] quartz is non-catalytic, but soft glass brings a mixture to equilibrium in a few hours. Alkalies act instantaneously.[10] A recent paper by Rumeau[16] concurs with the above in general, but he finds that phthalic anhydride is not a stabilizer, nor is a residue from the distillation of an ester previously treated with oxalic acid. Yet he notes that oxalic acid is an energetic stabilizer.

Apparatus and Experimental Method

To obtain the aseptic conditions mentioned by Meyer and, if possible, to improve on them, we planned to distil the ester in accordance with the method first used by Martin. The final form of our apparatus is shown in Fig. 1. This simple form of apparatus gave quite as good results as very much more complicated forms in which elaborate precautions were taken to prevent any possible contamination of the ester. The tubes A and B were connected to the apparatus by pieces of Gooch tubing. The

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[15] Dunstan and Mussel, *J. Chem. Soc.*, **99**, 566 (1911).

[16] Rumeau, *Bull. soc. chim.*, **35**, 762 (1924).

[17] Meyer and Willson, *Ber.*, **47**, 832 (1914).

tubes could therefore be easily removed and transferred to a thermostat for rate measurements. Our distillations were performed at pressures of 10^{-3} to 10^{-5} mm. of mercury. By keeping tube B at −78° and tube A at room temperatures, or a little higher, satisfactory rates of distillation were obtained. When distillation was completed we allowed air to enter the apparatus, the air having first been bubbled through sulfuric acid and then passed through an asbestos filter to remove acid mist and other suspended particles.

Analytical and Materials.—We found the analytical procedure perfected by Kurt Meyer[11] very satisfactory and used it without any important modifications throughout the work. We avoided as far as possible the use of violent cleaning reagents on our glass apparatus; our usual method was to give a final rinse in distilled water followed by heating nearly to the melting point. The acetoacetic ester used in our experiments was a commercial sample which we washed several times with distilled water, dried with calcium chloride and anhydrous copper sulfate and distilled; only the middle portion was used in our work.

Calculation of Rates.—In order to compare the stability of samples of ester prepared in different ways, it was necessary to measure the velocity constant of the change enol ⟶ keto.[10] Let x be the mole fraction of enol in any mixture and $1 - x$ the mole fraction of keto. Let k_1 be the rate of change of pure enol and k_2 the rate of change of pure keto. Then in any mixture, we have

$$\text{rate of change of enol to keto} = k_1x, \text{ and}$$
$$\text{rate of change of keto to enol} = k_2(1 - x)$$

Therefore,

$$-\frac{dx}{dt} = k_1x - k_2(1 - x)$$

If we put $k_1/k_2 = \alpha$ and integrate, we obtain

$$k_1 = \frac{\alpha}{t(1 + \alpha)} \ln \frac{x_0 - 1/(1 + \alpha)}{x - 1/(1 + \alpha)}$$

Throughout our work we took $\alpha = 11.82$, so that this equation becomes

$$k_1 = \frac{2.12}{t} \log \frac{x_0 - 0.078}{x - 0.078}$$

For ease of comparison of different samples we found it convenient to calculate a quantity that we refer to as the "half life," namely, the calculated time taken for a sample of pure enol to become a mixture of 50% enol and 50% keto. This is given by the formula

$$t_{1/2} = \frac{0.72}{k_1}$$

Experimental Results

In our earlier experiments extreme precautions were taken to prevent contamination of the ester, even to the extent of building the apparatus of fused silica. We finally found that we could relax these precautions and, in particular, use Pyrex glass instead of silica. Our first quantitative experiments were directed toward testing out the velocity equation which we have developed in the previous section. A sample of the ester was distilled in the apparatus shown in Fig. 1. The distillate was placed in a thermostat and samples were withdrawn for analysis at noted time intervals. A few of the results are given in Table I. It will be seen that k_1 shows a fairly satisfactory constancy over a period of several hundred hours.

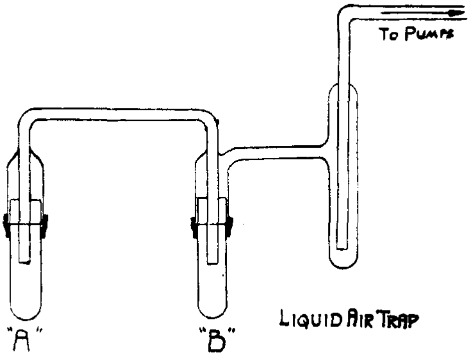

Fig. 1.

During this time, the tubes were opened many times to withdraw samples for analysis.

Our next experiments were directed toward finding if it were possible to transfer the ester from one container to another without contamination (Table II). The experiments usually show a fall in stability but the effect is not very great.

TABLE I

TABLE OF RESULTS

Sample A

Hours........	0	43	47.3	71.5	74.5	142.5	185	236	286	330
Enol, %	36.4	30.1	30.4	28.6	27.6	23.7	20.3	17.7	15.8	14.2
$k_1 \times 10^{-4}$	..	53	46	41	45	38	41	41	41	42

Sample B

Hours........	0	49.5	92.3	143.3	190.5	237.5	290.5	335	384
Enol, %	35.3	32.1	29.1	25.7	22.7	19.8	17	14.2	11.7
$k_1 \times 10^{-4}$	..	23	26	28	30	32	39	40	47

Sample C

Hours........	0	71.8	145.5	215.8	264.3	333.3	383.5	478.3	506
Enol, %	36.6	27.7	21.5	17.4	15.2	13.0	12.1	10.6	10.0
$k_1 \times 10^{-4}$		47	47	47	47	47	46	45	47

Sample D

Hours........	0	20.6	68.8	137.3	187.3	255.8	307.3	401.3
Enol, %	23.3	22.4	19.6	15.9	15.0	13.5	12.4	9.9
$k_1 \times 10^{-4}$	..	26	36	44	37	35	36	45

TABLE II

EFFECT OF TRANSFERENCE ON STABILITY OF ESTER

	Series A (Pyrex)				Series B (Quartz)			
Half life before transf.	175	175	175	175	131	131	131	131
Half life after transf.	156	161	151	158	108	124	116	150
Hours observed	17	17.5	18	18.5	545	470	470	640

In Series A the ester was transferred from a Pyrex container to four other Pyrex containers using a Pyrex pipet; in Series B from a Pyrex container to four quartz containers using a quartz pipet.

Series B is instructive because it shows that there is comparatively little difference in stability whether the ester is kept in quartz or Pyrex.

We made three runs in soft glass containers. The results are shown in Table III, which illustrates the great catalytic power of soft glass.

Table III

Rate of Change of Ester in Soft Glass

Init. enol, %	k_1	Half life	Hours obs.
18.7	1.76	24 min.	1.4
18.7	2.66	16 min.	1.2
17.3	7.58	6 min.	0.8

From our experiments with different kinds of containers we concluded that any catalytic surface action in quartz or Pyrex was small compared to the effect of impurities dissolved in the ester. We therefore turned our attention to removing traces of dissolved impurities. Table IV shows the results obtained when we distilled a large portion of ester and examined the stability of the successive fractions.

Table IV

Results on Fractionated Ester

Frac.	Initial enol, %	k_1	Half life	Hours obs.
1	41.5	0.021	34	286
2	32.4	.032	21	165
3	22.6	.055	13	165
4	12.1	.140	5	20
5	38.4	.0014	515	335
6	34.8	.0058	124	424
7	32.0	.012	61	330
8	31.6	.004	180	422

It will be seen that the stability increases as the distillation progresses, with possibly a maximum at the middle portions. Our experiments so far indicate that more efficient fractionation would result in a considerably diminished rate of isomerization. The erratic results shown by fractions 4 and 7 (in this particular experiment) are probably due to accidental contamination of some kind or other.

We next turned our attention to the addition of substances to the ester with the hope of stabilizing it. Our experiments in this direction, however, did not meet with any success. The addition of small quantities of substances like phthalic anhydride, oxalic acid and acetyl chloride, whether before or after distillation, had the effect of increasing the rate of change instead of diminishing it. The observed rate of change is probably largely due to the presence of a minute trace (a few parts per million of ester) of aminic impurities, and a trace of acetyl chloride might be expected to remove these.[18] However, further consideration shows that a small trace

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[18] See Lowry and Magson, *J. Chem. Soc.*, 93, 107 (1908).

of water present would hydrolyze the acid chloride probably at a faster rate than the latter would react with the aminic impurity. The removal of the last traces of water from a substance like acetoacetic ester is a difficult matter since violent dehydrating agents will decompose the ester. We tried the effect of activated silica gel on the ester, but there was obvious decomposition, the ester becoming brownish-red. The distillate from this had a half life of about one hundred hours.

In our final experiments we decided to add various substances in known amounts, and compare the rate of isomerization of the ester before and after this addition. The results are shown in Table V. The third column contains a list of the ratios of the rates k_2/k_1, where k_2 is the rate after addition of the catalyst, and k_1 is the rate before addition.

TABLE V

EFFECT OF CATALYSTS ON THE RATE OF ISOMERIZATION OF ACETOACETIC ESTER

Catalyst	Conc. $\times 10^{-5}$	k_2/k_1	Catalyst	Conc. $\times 10^{-5}$	k_2/k_1
Piperidine	4	11,400	Phthalic anhydride	40	6
Ammonia	4	4,000	Oxalic acid	1	3.2
Pyridine	4	264	Water	100	1
Quinoline	4	17	Dehydracetic acid	4	36
Bromine	4	>1,300	Residue	4	3
Acetyl chloride	4	157			

The extraordinary effect of small quantities of bases is at once apparent. Thus, one part in a million of piperidine increases the rate by three orders. It is somewhat surprising to find that bromine is an extremely good catalyst, being even more effective than some of the bases. Occasionally in the course of our work we would meet with very anomalous behavior which we may ascribe to accidental contamination since it is obviously very difficult to make quantitative measurements with materials so sensitive to small traces of basic substances.

We also made a study of the temperature coefficient of the rate of change of the liquid ester, since this does not seem to have been measured by previous workers. Measurements by Meyer[10] for aqueous solutions of the ester gave $k_{10}/k_0 = 3$, and by Meyer and Willson[17] for alcoholic solutions gave $k_{25}/k_0 = 1.3$. We made measurements on two samples at 25 and 35°, and obtained for k_{35}/k_{25} the values 4.9 and 6.3. Taking a mean value of 5.6 we obtain the value of 31,200 for the heat of activation. This is surprisingly large, especially when we compare it with the value for the aqueous solution.

Summary

1. We have made a quantitative study of the rate of isomerization of acetoacetic ester in the liquid condition. Distillations were carried out in high vacuum and every precaution was taken to prevent contamination of the ester.

2. The rate of change of the enolic form of the ester when prepared in this way was over 10 times slower than the (calculated) best values previously reported.

3. The velocity constants for the change have been measured in presence of known amounts of various substances.

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FLUOSILICATES OF SOME ORGANIC BASES[1]

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Introductory

It is well known that fluosilicic acid is a relatively strong acid which yields insoluble salts with most inorganic bases, a large number of which have been prepared. However, few attempts have been made to prepare the salts of this acid with organic bases. E. Ebler and E. Schott[2] have described a fluosilicate of hydrazine, $N_2H_4 \cdot H_2SiF_6$, and of hydroxylamine, $(NH_2OH)_2 \cdot H_2SiF_6$. On the other hand, a number of hydrofluorides of organic bases have been isolated and found to be well-defined, crystalline compounds. Weinland and Lewkowitz[3] report upon the hydrofluorides of aniline, aminophenol, aminophenetole, aminobenzoic acid, etc.

This paper describes the preparation and properties of fluosilicates of aniline, methylaniline and *o*-, *m*- and *p*-toluidine.

Experimental

For the preparation of the aniline salt, redistilled aniline, dissolved in about three times its volume of 95% ethyl alcohol, was treated with a 30% aqueous solution of fluosilicic acid in such a way that the aniline was kept in excess. The precipitated product was washed free from excess aniline with cold 95% ethyl alcohol. The precipitate was then recrystallized twice from hot 95% alcohol and dried, first in the air and finally in a desiccator over sulfuric acid.

The product thus prepared was found to be a snow-white powder composed of small plate-like crystals of irregular shape. Upon heating it sublimed, the sublimation being rapid at a temperature of about 230°. It was insoluble in absolute ethyl alcohol, methyl alcohol, acetone, carbon tetrachloride, chloroform, ethyl ether and carbon disulfide, slightly soluble in hot acetone, but extremely soluble in water. When heated a gas was evolved which when passed into water caused the precipitation of gelati-

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[1] In memory of Ira Remsen.

[2] Ebler and Schott, *J. prakt. Chem.*, [2] **78**, 338 (1908); [2] **81**, 552 (1910).

[3] Weinland and Lewkowitz, *Z. anorg. Chem.*, **45**, 39–51 (1905).