vided into two groups depending on whether their spectra resemble that of styrene or of *trans*-stilbene. *cis*-Stilbene, which has a spectrum intermediate in character between the two types, is the only exception to this generalization. An explanation of this optical behavior is offered, based on a consideration of the steric factors which interfere with the attainment of the most stable resonance structures.

KINGSTON, CANADA RECEIVED MAY 24, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Rates and Temperature Coefficients of the Hydroxyl Ion Catalyzed Aldol Condensation of Benzaldehyde with Methyl Ethyl Ketone and Acetone[1]

BY JOSEPH D. GETTLER AND LOUIS P. HAMMETT

In principle and in fact,[2] a symmetrical ketone such as acetone may condense with one mole of benzaldehyde in only one way to form a primary condensation product, benzalacetone. On the other hand, it is possible for an unsymmetrical ketone, such as phenylacetone or methyl ethyl ketone, to condense with one mole of benzaldehyde to yield two isomeric ketones. Goldschmidt[3] studied the reaction between phenylacetone and benzaldehyde and reported that in acid medium stibyl methyl ketone was formed while in alkaline medium cinnamyl benzyl ketone was formed. Levinstein[4] reported that in alkaline media the methyl ethyl ketone condensation occurred at the methylene carbon. He made no mention, however, of the formation of an isomeric compound formed in acid media. In contradistinction to this Müller and Harries[5] showed that in alkaline solutions a compound which they named alpha-benzalmethyl ethyl ketone is formed while in acid media the isomeric gamma compound is formed. Ryan and Devine[6] and Massara and Di Leo[7] concerned themselves chiefly with the study of the reaction products involving more than one mole of benzaldehyde. Not one of the above-mentioned investigators, however, studied the reaction with a view of finding conditions under which the primary reaction products would be produced alone to the exclusion of higher products.

Nikitin[8] followed kinetically the reaction of benzaldehyde with acetone and reported that the aldehyde is involved to the second power in the kinetic equation while Coombs and Evans[9] studied the reaction between acetophenone and benzaldehyde and showed it to be kinetically bimolecular, the velocity also being proportional to the concentration of the catalyst. Bell[10] found the aldolization of acetaldehyde to be first order with respect to the aldehyde and approximately a linear function of the catalyst. All these investigations were concerned with the base catalyzed reaction.

Since the authors of the present paper were primarily interested in the mechanism and kinetics of formation of the isomeric primary condensation products of the methyl ethyl ketone reaction, it was essential to repeat all the past synthetic work in order to establish under just what conditions one may obtain a reaction yielding only primary condensation products with no higher products or resins and to select a suitable solvent for the kinetic experiments.

Experimental

Synthetic Part.—The earlier workers[5,6,7] in the field reported besides the two primary condensation products, (A) α-benzalmethyl ethyl ketone and (B) γ-benzalmethyl ethylketone, the existence of several other higher condensation products. These include (C) $C_{18}H_{18}O_2$, 1,5-diphenyl-4-methyl-pentene-1-one-3-ol-5; (D) $C_{25}H_{20}O$, tribenzalmethyl ethyl ketone; (E) $C_{18}H_{17}OCl$, 1,5-diphenyl-4-methyl-5-chloropentene-1-one-3.

The synthetic work of Müller and Harries[5] involving the acid and base catalyzed reaction between benzaldehyde and methyl ethyl ketone was repeated in detail during the present research. Its scope was materially extended by studying the effect of the initial concentration of the reactants on the nature and yield of the products. The experimental results are presented in tabular form.

From the data in Tables I and II the following conclusions may be drawn: (1) In both the acid and base condensations, as the ratio of aldehyde to ketone approaches

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(1) Dissertation submitted by Joseph Daniel Gettler in partial fulfillment of the requirements of the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

(2) Claisen and Ponder, *Ann.*, **223**, 139 (1884).

(3) Goldschmidt and Krczmar, *Monatsh.*, **22**, 657 (1901); Goldschmidt and Knopfer, *ibid.*, **18**, 437 (1897); **19**, 406 (1898).

(4) Levinstein, Inaug. Diss., Berlin, Jan. 29, 1902.

(5) Müller and Harries, *Ber.*, **35**, 966 (1902).

(6) Ryan and Devine, *Proc. Roy. Irish Acad.*, **32**, 208 (1916).

(7) Massara and Di Leo, *Gazz. chim. ital.*, **63**, 199 (1933).

(8) Nikitin, *J. Gen. Chem.* (*U. S. S. R.*), **7**, 9 (1937).

(9) Coombs and Evans, *J. Chem. Soc.*, 1295 (1940).

(10) Bell, *ibid.*, 1637 (1937).

TABLE I

ALKALINE REACTION

Molar ratio aldehyde/ketone	Catalyst	Solvent	% A	% C	% Acid benzoic	% Resin[a]
0.5	NaOH	Water	99	..	..	...
1	NaOH	Water	93	4	..	Trace
2	NaOH	Water	25	29	16	Large
1	NaOH	C_2H_5OH	5	45	..	Large

[a] The amount of resin formation was only approximated.

TABLE II

ACID REACTION

Molar ratio aldehyde/ketone	Catalyst	Solvent	% B	% E	Amount of resin[a]
1	HCl gas to	None	94	0	Trace
2	saturation	None	60	0	Large

unity and is permitted to assume a value less than unity the yield of primary products increases progressively at the expense of the higher molecular weight compounds. (2) Alcohol promotes the formation of the higher products, thus making it an unsuitable medium for kinetic studies.

The alpha compound melts at 38.0° and the gamma compound melts at 38.1°. The non-identity of these compounds was confirmed by the preparation of suitable derivatives. It has been previously reported[5] that a mixture of equal amounts of these two compounds exhibited no melting point depression. This statement was not substantiated as indicated by the following data.

TABLE III

% Alpha compound	% Gamma compound	Melting point, °C.	Depression, °C.
0	100	38.1	..
25	75	31.2	6.9
50	50	15.0	23.1
75	25	32.5	5.6
100	0	38.0	..

Ryan and Devine[6] studied the conditions of formation of the higher condensation products and reported that compound D was formed when benzaldehyde reacted with methyl ethyl ketone in alcohol under the influence of an acid catalyst. All their reported findings were confirmed during the present research. Massara and Di Leo[7] investigated the effect of the concentration of the acid catalyst on the course of the reaction but their paper gave few details as to the exact experimental conditions and yields.

TABLE IV

ACID CONDENSATION

Molar ratio aldehyde/ketone	Catalyst	% B[a]		% E[a]		Resin
		M	GH	M	GH	
1	HCl gas to	+	94	−	−	Trace
2	saturation	−	60	+	−	Large
1	HCl gas to be-	−	48	+	18	Large
2	yond satn.	−	30	+	25	Large

[a] M refers to results of ref. 7; GH refers to results of present paper; − compound reported as not formed; + compound reported as formed.

A comparison of their findings with those of the present investigation are listed in Table IV.

From the values of Table IV it may be seen that the nature of the reaction products is a function both of the initial reactant concentrations and of the concentration of the catalyst. In an attempt to prepare compound C by the alkaline condensation of benzaldehyde with compound A in alcoholic solution, there was obtained a heretofore unreported compound whose analysis and molecular weight indicated the empirical formula $C_{14}H_{14}O$. All group characterization tests were negative and the exact structure is as yet unknown.

Kinetic Part

Apparatus.—Only calibrated weights and volumetric apparatus were used. The temperatures were determined by thermometers calibrated by the Bureau of Standards. The thermostats used at 25 and 50° were of the conventional type.

Materials.—**Methyl ethyl ketone** (Eastman Kodak Co. White Label) was refluxed over potassium permanganate until no positive aldehyde test could be obtained with Schiff reagent. It was then dried by refluxing over phosphorus pentoxide for twelve hours, fractionated through an eight-bulb all-glass distilling column taking all precautions to exclude moisture. Only the middle fraction (b. p. 79.5–80.5°) was retained. The receiver was removed from the distilling apparatus and immediately closed with a two-holed cork stopper, through one hole of which was admitted a rapid stream of dry oxygen-free nitrogen. A fifty-cc. Becton and Dickinson ground-glass hypodermic syringe fitted with a five-inch stainless steel hypodermic needle was used to withdraw and transfer the ketone to 10-cc. Jena amber glass ampules, which had been previously dried and flushed with pure nitrogen. The ampules were immediately sealed and stored for future use.

Acetone (Eastman Kodak Co. White Label) was refluxed over potassium permanganate and calcium oxide for eight hours and then distilled from an all-glass apparatus. The fraction of b. p. 56–56.5° was retained and stored in glass ampules as in the case of methyl ethyl ketone.

Benzaldehyde (Eastman Kodak Co. Chlorine Free) was first vacuum distilled in an atmosphere of pure nitrogen and then dried over calcium chloride. The dry product was then twice vacuum distilled in an inert atmosphere using an all-glass apparatus. In the final distillation the fraction of b. p. 74–76° at 16 mm. was retained. Care was taken to exclude air and moisture and the product was stored as in the case of methyl ethyl ketone.

Hydroxylammonium sulfate (Commercial Solvents Corp.) was twice recrystallized from 50% methyl alcohol, air dried and then dried in a vacuum desiccator.

Dioxane.—1,4-Dioxane (Carbide and Carbon Chemical Co.) was purified in 3–4-liter quantities as described by Beste and Hammett.[11]

Indicator Solution.— 0.1% phenol blue (tetrabromophenolsulfonephthalein) solution in 30% ethyl alcohol.[12]

Colorimetric Experiments.—Considerable time was spent in trying a Schiff colorimetric aldehyde method to follow the kinetic reaction using a Leitz photoelectric

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(11) Beste and Hammett, THIS JOURNAL, **62**, 2481 (1940).

(12) Schultes, *Z. angew. Chem.*, **47**, 258 (1934).

colorimeter. It was found, however, that while ketones do not react with the reagent itself, they do affect the rate of color development caused by the aldehyde to such an extent that a precise determination is impossible.

Acid Reaction.—Several attempts were made to follow the acid-catalyzed reaction between methyl ethyl ketone and benzaldehyde. It was observed, however, that as the reaction proceeded, the carbonyl content apparently increased instead of decreasing as it should do normally. No explanation of this fact could be found.

Method.—The rate of reaction was followed by the analytical method of Schultes[12] which is based on the fact that carbonyl compounds react with hydroxylammonium sulfate to form oximes and to liberate sulfuric acid, which may be determined readily by an acidimetric titration. The procedure is as follows. To 10 cc. of an 8% solution of hydroxylammonium sulfate containing 5 drops of a 0.1% solution of brom phenol blue, there is added a definite volume of the reaction mixture. The resulting solution is well agitated and allowed to stand at room temperature to ensure complete reaction. At the end of this period the solution is titrated with standard base.

In applying this analytical method to the problem at hand it was found that benzaldehyde and methyl ethyl ketone react almost instantaneously with the reagent to yield oximes. On the other hand, alpha-benzalmethyl ethyl ketone and benzalacetone react slowly and, therefore, to ensure complete reaction, a standing time of at least an hour was necessary.

The end-point of the titration is not very sharp in water-dioxane mixtures and considerable experience is required for its recognition. The acid solution is yellow and upon progressive neutralization becomes green, blue-green and finally blue. To obtain consistent and reproducible results it was necessary to compare all titrations with a standard known blank. The blank was identical with the samples in all respects except that it contained no carbonyl compounds but did contain enough standard base to give it the blue color characteristic of the end-point. The samples were titrated to this blue color. Typical analyses are presented in Table V.

The solvent in the kinetic experiments was a mixture of 70% dioxane and 30% water by weight except in those instances where its concentration was varied to study medium effects. In all cases the sodium hydroxide was introduced as a solution at the time the solvent was prepared, and correction was made for the amount of water displaced by this solute.

TABLE V

ANALYTICAL DETERMINATIONS

Compound or mixture	Amount present, mg.	Moles of carbonyl	No. of analyses	Amount found	% Error
Benzaldehyde	57.77		6	56.97	−1.4
	41.89		3	42.55	+1.3
Methyl ethyl ketone	36.06		5	36.05	−0.02
	72.56		4	72.68	+0.16
Alpha compd.	39.97		7	40.60	+0.63
Gamma compd.	82.59		5	82.15	−0.54
Acetone	58.96		3	59.10	+0.10
Benzalacetone	74.98		3	75.07	+0.12
Benzaldehyde	100.51	0.2752	3	0.2793	+1.5
Methyl ethyl ketone	30.98				
Same	97.49	.2821	3	.2812	−0.3
	35.54				
Same	40.19	.1878	4	.1898	+1.1
	34.44				
Benzaldehyde	19.07	.6567	6	.6415	−2.1
M. E. K.	16.12				
γ-Compound	40.59				
Benzaldehyde	97.10	.4582	4	.4625	+0.95
M. E. K.	81.10				
α-Compound	40.30				
Benzaldehyde	26.82	.1260	4	.1277	+0.14
acetone	58.59				

Since benzaldehyde is so prone to oxidation, it was impractical to make up standard stock solutions and use them for the kinetic experiments. Hence reaction charges were prepared in the following manner. Two-cc. amber Jena glass ampules were initialed with a diamond pencil, cleaned, dried and weighed. Then pure benzaldehyde, of approximately the required weight, was introduced by means of a 1-cc. hypodermic syringe into the ampules, which had been previously flushed with pure dry nitrogen. The ampules were immediately sealed and weighed. Ampules were selected at random and the purity tested by the method of Eitel and Lock[13] by 2,4-dinitrophenylhydrazone of benzaldehyde and determining it gravimetrically. Benzaldehyde preserved according to the above procedure showed no discernible oxidation over a period of six morths. In a similar fashion samples of the other reactants were prepared.

In starting experiments the reaction bottle containing the catalyst solution was placed in the thermostat to reach temperature equilibrium. The weighed charges of reactants, contained in ampules, were placed in the reaction bottle, the latter was shaken to break the ampules and samples were removed at convenient intervals for analysis.

Rate Calculations.—In basic medium, when the concentration of the ketone is initially greater than the concentration of benzaldehyde, the following reactions occur in the cases of methyl ethyl ketone and acetone.

$$C_6H_5CHO + CH_3COC_2H_5 \longrightarrow C_6H_5CH{=}CHCOCH_2CH_3 + H_2O \quad (I)$$

$$C_6H_5CHO + CH_3COCH_3 \longrightarrow C_6H_5CH{=}CHCOCH_3 + H_2O \quad (II)$$

Hence, if a denotes the initial concentration of ketone, b the initial concentration of aldehyde and x the concentration of product formed in time t, then the concentration of aldehyde is $(b - x)$, that of ketone is $(a - x)$ and the total carbonyl content at this time is $(a + b - x)$. The analytical reaction is given by the equation

$$2 >CO + (NH_2OH)_2 \cdot H_2SO_4 \longrightarrow 2 >C{=}N{-}OH + H_2O + H_2SO_4$$

from whence it follows that the volume of stand-

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(13) Eitel and Lock, *Monatsh.*, **72**, 385 (1939).

ard base required to neutralize the liberated sulfuric acid of any sample will be proportional to the total carbonyl content. As reaction (I) or (II) proceeds it is evident that successive samples of the reaction mixture will exhibit a progressive decrease in carbonyl content. Knowing the value of $(a + b - x)$ we may readily determine $(a - x)$ and $(b - x)$ and using the second order reaction equation calculate k. In practice the specific rate constant was obtained by plotting $1/(a - b) \ln (a - x)/(b - x)$ against t.

The deviation of the mean of the rate constants was taken as the precision measure of the average as the reproducibility was considered a better measure of the accuracy of the constant than the probable error in the least squares slope of any individual measurement. This error ranged from 3 to 6%.

Results.—The kinetic experiments were followed in practically all cases to at least 55% completion. It was not always possible to follow them further, with any degree of precision, because of the following reasons. First, as the reaction proceeded, the increased concentration of product often caused an immediate precipitation of solids when the kinetic sample was added to the analytical reagent and, secondly, the oxime of the reaction product often precipitated as its concentration increased in the analytical mixture. These precipitations prevented an accurate titration. Dioxane was usually added to redissolve the solids, but the resultant increased volume still made for a less accurate determination.

From the data listed in Table VII it may be observed that the variation of the concentrations of the reactants and catalyst is rather limited. These restrictions were imposed by the necessity of (1) maintaining the concentration of ketone always in excess to that of the aldehyde and (2) selecting dioxane–water solutions of such concentrations that only homogeneous mixtures of catalyst and reactants resulted throughout the whole course of the reaction.

TABLE VI

SAMPLE DATA: BASE-CATALYZED ADOLIZATION OF BENZALDEHYDE WITH METHYL ETHYL KETONE

Medium: 70% dioxane, 0.03605 M NaOH; temp. 50°C.; initial concentrations: benzaldehyde 0.02513 M, methyl ethyl ketone 0.1009 M; standard base 0.05170 M NaOH; 10-cc. (corrected) samples; time in minutes.

Time, minutes	Cc. base used	Concn. product, M	k
15	16.98	0.00224	0.0622
30	16.69	.00393	.0571
45	16.22	.00620	.0641
60	15.94	.00765	.0622
75	15.64	.00920	.0630
90	15.40	.01044	.0624
105	15.20	.01148	.0612
		Av.	.0617

TABLE VII

t, °C.	% Dioxane	[NaOH]	[Ketone]	[Aldehyde]	No. of detns.	$k \times 10^2$
50	70	0.05292M	0.1010M	0.02530M	1	7.84
50	60	.05292	.1010	.02530	2	7.76
50	50	.05292	.1010	.02530	1	7.78
50	70	.05019	.1008	.02516	3	7.31
50	70	.03605	.1009	.02513	1	6.17
50	70	.02487	.1008	.02519	1	4.83
50	70	.01226	.1008	.02516	4	3.26
50	70	.00435	.1008	.02516	2	1.73
50	70	.00000	.1009	.02517	1	..
50	70	.05080	.1248	.02500	4 (7)	7.56
50	70	.05080	.1003	.02500	2 (6)	7.26
50	70	.05080	.0748	.02500	3 (8)	7.14
50	70	.05080	.1280	.03005	2 (2)	7.86
50	70	.05080	.1129	.03005	1 (2)	7.62
50	70	.05080	.0875	.03005	2 (3)	7.38
50	70	.05080	.1125	.05005	2 (2)	8.00
50	70	.05080	.1000	.05005	3	7.92
50	70	.05080	.0812	.05005	1 (2)	7.79
50	70	.05000	.1003	.05005	1 (9)	7.87
50	70	.05000	.1003	.03003	3 (5)	7.52
50	70	.05000	.1003	.02510	3 (8)	7.37
50	70	.05000	.1003	.01001	2 (8)	7.09
50	70	.05000	.1248	.05000	2 (3)	7.98
50	70	.05000	.1248	.03250	1 (1)	7.68
50	70	.05000	.1248	.02500	3 (2)	7.51
50	70	.05000	.1248	.01000	2 (1)	7.21
50	70	.05000	.0748	.04500	1 (1)	7.49
50	70	.05000	.0748	.02500	2	7.09
50	70	.05000	.0748	.03810	2 (1)	7.37
50	70	.05067	.1000	.02550	3	7.54
25	70	.05067	.1000	.02550	2	4.01
			Acetone Reaction			
50	70	.05067	.1001	.02518	4	28.0
25	70	.05067	.1001	.02515	3	10.0
25	70	.03605	.1002	.02514	2	8.2

Energies of Activation

Compound	Temp. range, °C.	E calories
Methyl ethyl ketone	25-50	4800
Acetone	25-50	7800

During the course of this research many kinetic experiments were followed in which the initial concentrations of one or both of the reactants were not exactly equal to the concentrations listed in Table VII. The specific rates of these odd concentration experiments were calculated back to what they would have been if the initial concentrations were of standard values. This conversion was carried out by graphical methods. In Table VII the number of these odd concentration experiments is given in parentheses in the column headed number of duplicate experiments. The values of the rate constants thus obtained were averaged with the constants of the standard concentration runs.

Discussion

The results of the present investigation indicate that the base catalyzed reaction of benzaldehyde with excess methyl ethyl ketone, in dioxane–water mixtures, is kinetically first order with respect to the concentrations of both aldehyde and ketone. On the other hand, the specific rate is proportional to the square root of the analytically determinable base concentration and is but slightly influenced by large variations in the water content of the solvent. All evidence points to the fact that the condensation is not reversible but proceeds to completion.

The data indicate the existence of pronounced medium effects with small changes in the nature of the medium except for the small effect of water, and the specific rates consequently vary with the initial concentration of the reactants. This change in specific rate exhibits a parallelism with change in the initial concentration of either reactant. For a five-fold increase in aldehyde concentration there is a 9% increase in the rate constant while a 70% increase in the initial concentration of the ketone gives rise to a 5% variance.

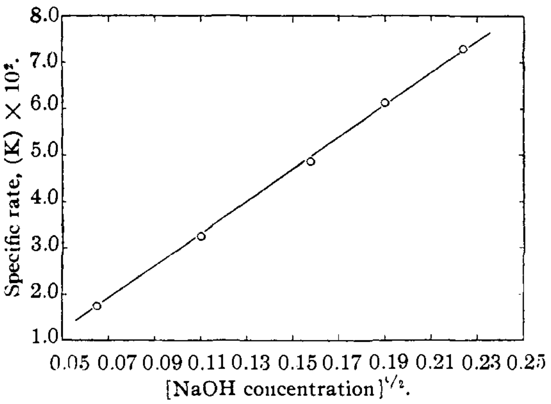

Fig. 1.—Effect of OH⁻ ion on specific rate.

Over the range of concentrations measured, the rate constant *k* varies, as shown in Fig. 1, linearly with the square root of the sodium hydroxide concentration. This relationship must, however, fail at lower concentrations, since it extrapolates to a negative value of the rate constant at zero concentration of hydroxide. The basis for the relationship is not clear, although it presumably results from some sort of partial compensation of the ion association of the sodium hydroxide by that of the sodium salt of the ketone, the association being smaller in the latter case because of the greater ion size.

Since an increase in water concentration would presumably increase the concentration of the catalytic hydroxyl ion, the small effect observed suggests the presence of some compensating influence of unknown nature.

The energies of activation of the two reactions studied are relatively small in magnitude as is common to other reactions of this type. In passing from a relatively simple molecule, acetone, to a more complex one, methyl ethyl ketone, we observe a very large decrease in the energy of activation, some 3000 calories, which is equivalent to a variation in *k* of some two orders of magnitude. The entropy of activation for aldolization in the case of the former compound is some 12 cal./deg. more positive than for the latter one. These results are in complete accord with the findings of Price and Hammett[14] concerning the effect of structure on the reactivity of carbonyl compounds. They likewise observed that, in the case of semicarbazone formation, the entropies of activation parallel the rigidity of the carbonyl compounds. The results of the present investigation may be satisfactorily explained on a theoretical basis[14] if it is assumed that the abovementioned parallelism indicates a transition state which possesses a relatively rigid molecular structure. If this is the case, it follows that a carbonyl compound, possessing many internal degrees of freedom, will lose most of these upon activation, while a more rigid structure cannot do so. This freezing out of internal motion results in a less positive entropy of activation with the less rigid carbonyl compounds.

The condensation under consideration is a typical base-catalyzed carbonyl addition reaction and undoubtedly possesses the following mechanism.[15] The base catalyst first removes a proton from the more acidic compound, in this case the ketone, to yield an anion, this proton exchange being reversible. The anion thus produced attacks the carbonyl group of the benzaldehyde in a rate determining step and the resulting ion in turn removes a proton from the conjugate acid of the catalyst forming the aldol product, which then undergoes a rapid dehydration.

This condensation is one which is very convenient to follow despite the limitations imposed by solubility considerations and the inherent nature of the reaction itself. Its rates are rapid

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(14) Price and Hammett, THIS JOURNAL, **63**, 2389 (1941).

(15) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 343.

enough so that considerable data may be obtained in a relatively short period of time yet not so rapid as to prevent accurate measurement. The temperature coefficient is sufficiently small to allow the use of a rather wide temperature variation, which makes for precision in the determination of energies and entropies of activation.

The authors wish to express their appreciation of the advice and assistance given by Professor R. C. Elderfield during the extended absence of one of them (L. P. H.).

Summary

The acid and base catalyzed aldolizations of benzaldehyde with methyl ethyl ketone have been studied synthetically in detail. It was found that concurrent and consecutive reactions may be totally eliminated by a careful selection of experimental conditions.

Kinetically, the base catalyzed reaction is first order with respect to the concentration of both aldehyde and ketone. The specific rate is linear in but not proportional to the square root of the analytically determinable concentration of the base. Medium effects are pronounced and the specific rate exhibits a parallelism to the initial concentration of either reactant.

The base catalyzed aldolization of benzaldehyde and acetone was also studied kinetically but in somewhat lesser detail.

Energy and entropy activation values lend additional support to the theory of Price and Hammett, concerning the effect of structure on the reactivity of carbonyl compounds.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, HARVARD UNIVERSITY]

The Radioactive Exchange and Adsorption of Methyl Bromide with Several Inorganic Bromides

BY G. B. KISTIAKOWSKY AND JOHN R. VAN WAZER

Introduction

In order to add some data to the fund of information which will some day lead to a complete, general theory of heterogeneous catalysis, a quantitative study was made of the exchange of bromine isotopes between radioactive methyl bromide and several inorganic bromides. Aluminum bromide, barium bromide and potassium bromide were used since the first is a strong catalyst for certain reactions of methyl bromide, the second is a mild catalyst, and the third does not exhibit catalytic activity. The adsorption of methyl bromide on barium bromide was investigated in order to elucidate the mechanism of the exchange. Adsorption studies were not made on aluminum bromide because of the complicating action of impurities such as aluminum hydroxide.

Materials.—The radioactive methyl bromide was prepared in the following manner so that the measured radioactivity was due to Br^{80} with a thirty-four-hour half-life. Bromoform containing a trace of bromine was irradiated by slow neutrons in the Harvard Cyclotron. The free bromine containing a large fraction of the bromine radioactivity was then completely extracted from the bromoform by means of a cold solution of ammonium hydroxide. In order to avoid any complication of the exchange process by high energy bromine atoms coming from the isomeric transition of Br^{80} (4.4 hr.) to Br^{80} (18 min.) and also to be able to neglect the natural decay rate of the radioactivity in the calculation of exchange rates, the ammonium bromide was allowed to stand for thirty-six hours before it was used. During this time the aqueous extractions were evaporated on a steam-bath to pure, dry ammonium bromide. This salt was mixed with sulfuric acid and methyl alcohol and heated in a small reaction flask so arranged that the evolved gases were passed through four absorption columns, the first of which contained water, the other three concentrated sulfuric acid. The resulting pure dry methyl bromide with radioactive bromine was condensed in a trap cooled by dry-ice.

The barium bromide crystals used in the exchange studies were prepared by fusing dehydrated commercial C. P. barium bromide in a platinum boat within a furnace made from a porcelain tube. When the barium bromide had melted, the temperature of the furnace was slowly reduced and the furnace was evacuated. The barium bromide was then cooled under vacuum to *ca.* 100°. The resulting fused mass (probably a single crystal) was ground up in a mortar kept at 150° and the powder was shaken through a set of brass sieves also at *ca.* 150°. By this means, grains of a definite size and reproducible geometrical surface were obtained. Microscopic study showed that these grains were all crystalline conchoidal fracture particles with no visible surface cracks or fissures. The seventy-mesh particles had an average area of 3×10^{-3} sq. cm. and an average volume of 1.2×10^{-2} cu. cm. per particle. The barium bromide that was used for adsorption experiments was hydrated and dehydrated a number