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THE REACTIVITY OF ATOMS AND GROUPS IN ORGANIC COMPOUNDS. VII. THE INFLUENCE OF CERTAIN SOLVENTS ON REACTION VELOCITY—ADJUVANCE

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It has long been known that the rate at which a reaction takes place in solution is markedly affected by the solvent. This fact has been studied by a number of investigators, but no adequate explanation has as yet been offered. The object of the work about to be described was not to attempt to solve this problem, but to get definite information in regard to the relative effects of the members of a series of alcohols on the rate at which a reaction took place in solutions in which the alcohols served as solvents.

In order to facilitate the consideration of the effects of solvents on reaction velocity, it seemed desirable to coin a new word which would serve to express this kind of action. The word *adjuvance*, from the Latin *adjuvans* from *adjuvare*, to help or to assist, has been found convenient in expressing the behavior of solvents from this point of view. For example, reactions, in general, take place more rapidly in nitrobenzene than in benzene; the adjuvance of the former is greater than that of the latter. It is impossible to measure the absolute adjuvance of a solvent but the word can be used in a derived sense to express quantitative relationships. We have found, for example, that the adjuvance of nitrobenzene is 26 times that of benzene when the reaction involved is that between pyridine and ethyl iodide. This means that the rates at which the reaction takes place in the two solvents are in the ratio of 26 to 1.

The desirability of studying the adjuvance of aliphatic alcohols is evident from the following facts. In most of the determinations of the rates at which alcohols enter into reaction with other substances, the alcohol studied has been used in excess as the solvent. This is notably the case in the large amount of work on rates of esterification. The values obtained are specific and express the behavior of the alcohol under the conditions of the experiment. They cannot be used in making absolute comparison between any two alcohols. The velocity of esterification, when measured in the way just indicated, is determined by the nature of the alcohol and its adjuvant effect. If the adjuvance of methyl alcohol is different from that of ethyl alcohol, the observed velocity constants of esterification of these alcohols with the same acid cannot be used to express the relative quantitative behavior of the alcohols in esterification. It has been found

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[1] In memory of Ira Remsen.

[2] From the thesis of Spencer Ward Prentiss, submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1925.

by several investigators that reactions, in general, take place more rapidly in methyl than in ethyl alcohol. It is probable that this difference in adjuvance exerts its effect in reactions in which the alcohols serve as both reactant and solvent.

In 1887 Menschutkin[3] discovered the phenomenon of adjuvance when he was investigating the rates at which certain alcohols react with acetic anhydride. The reaction was carried out in an "indifferent" solvent, benzene. When xylene and hexane were used in place of the latter he was surprised to find that the rates observed were not the same as before. This led to a detailed study of the subject.[4]

No systematic study of the adjuvance of alcohols has been made. As such information was needed in the interpretation of the results of work being carried out in this Laboratory, eight alcohols were examined. In addition, the adjuvance of nitrobenzene, acetone and benzene were determined.

In order to reduce experimental difficulties to a minimum and obtain results that would probably be susceptible of interpretation, a comparatively simple reaction was first studied—the addition of ethyl iodide to pyridine.

Especial care was taken in the purification of the substances used. The effect of concentration of the reactants on the velocity constant was found to be small within the limits studied, 0.23 and 1.0 *M*. In Table I are given the results obtained.

TABLE I

SECOND ORDER VELOCITY CONSTANTS OF THE REACTION PYRIDINE + ETHYL IODIDE = ETHYL PYRIDONIUM IODIDE

Temp., 25.00°. Time in hours

Solvent	Velocity constant	Relative values, Benzene = 1	Solvent	Velocity constant	Relative values, Benzene = 1
Benzene	0.0028	1	*n*-Propyl alcohol	0.0031	1.11
Nitrobenzene	.070	25.0	*n*-Butyl "	.0031	1.11
Acetone	.036	12.8	*Iso*propyl "	.0030	1.07
Methyl alcohol	.0070	2.50	*Sec.*-butyl "	.0028	1.00
Ethyl "	.0039	1.40	*Tert.*-butyl "	.0026	0.93

The results show that nitrobenzene and acetone have a high adjuvance relative to that of benzene. Menschutkin found in the study of the reaction between trimethylamine and ethyl iodide at 100° the value 10.4 for acetone, whereas with pyridine and ethyl iodide at 25° we find 12.8. He did not study nitrobenzene.

Methyl alcohol has a distinctly higher adjuvance than ethyl alcohol, which in turn is higher than *n*-propyl alcohol. Further increase in molecular weight has little or no effect. It is a striking fact that the adjuvance

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[3] Menschutkin, *Z. physik. Chem.*, **1**, 611 (1887).

[4] Menschutkin, *ibid.*, **5**, 589, and **6**, 41 (1890).

of tertiary butyl alcohol is so close to that of the isomer with the normal structure. The two alcohols differ widely in chemical properties. It is also noteworthy that the adjuvance of these oxygen compounds approaches so closely that of benzene. The facts suggest that adjuvance may be related more to physical forces set up between the molecules involved than to chemical attractions.

The only previously determined values with which the results here given can be compared are those obtained by Menschutkin. In his study of the reaction between trimethylamine and ethyl iodide at 100°, he used a variety of solvents, among which were benzene, methyl alcohol and ethyl alcohol. His values for these substances are, respectively, 1, 8.8 and 6.3. Results at 100° are not strictly comparable with those at 25°. Further, it is highly probable that at 100° a reaction takes place between the alcohols and ethyl iodide, as a result of which hydriodic acid is liberated. Any ionizable iodine formed in this way would have been included in the analyses made and calculated as produced in the primary reaction. We are convinced that this error came into the work, because it has been found in this Laboratory that *n*-butyl bromide reacts at a measurable rate at 100° with *n*-butyl alcohol to form the ether and hydrobromic acid. The relative adjuvance of the two alcohols measured at different temperatures and by means of different reactions with the possible source of error just indicated are in the two sets of experiments 1 to 1.8 and 1 to 1.4.

No results have been reported in regard to the other alcohols with which ours can be compared. It is planned to study the adjuvance of these alcohols in a reaction of a different type to see to what extent the nature of the reaction affects the results. The values that have been obtained will be used in the interpretation of the results of experiments which will be published later.

Experimental Part

The determinations of the velocity constants were made in the following manner. Equimolecular quantities of the reactants were added to the amount of the solvent necessary to produce a solution of the desired concentration. Measured amounts of the mixture were then placed in ampules, which were sealed and put into a thermostat at 25.00°. The time at which the second reactant was added was taken as zero. This was justifiable because the reaction was a very slow one and the temperature of the solutions before being placed in the thermostat was close to 25°. The first analyses made at the end of about half an hour showed that the reaction had taken place to less than 0.5%.

From time to time an ampule was broken under water. The solution was acidified with nitric acid, silver nitrate was added and the excess of the latter was titrated with a solution of potassium thiocyanate. Check titrations of solutions in different ampules frequently agreed to within 0.5%. All the measuring apparatus used was carefully calibrated and care was taken to prevent contamination from the moisture of the air.

Second order velocity constants were calculated in the usual way. It was found that the values obtained as the reaction proceeded slowly increased. In order to get the true constant these values were extrapolated to zero time, using the following method. The values of t and of k were separated into two groups as nearly equal as possible. The average values of t and k in each group were computed, and from the differences between the t values and between the k values was obtained a linear equation in t and k. The value sought is the value of k when t is placed equal to 0. This method will be seen to be the two point method of obtaining the equation of a straight line.

In Table II are given the data used in a typical experiment.

Table II

The Velocity Constant of the Reaction between Pyridine and Ethyl Iodide Dissolved in *n*-Propyl Alcohol

$d_{4°}^{25°} = 0.7998$. Time in hours

	Moles	G.	No.	Time	Fraction converted	K
Propyl alcohol		34.998	(0)	0.5	0.002	.....
Pyridine	0.0350	2.771	1	24	.054	0.00336
Ethyl iodide	.0350	5.459	2	24	.055	.00342
			3	72	.153	.00356
Solution		43.228	4	72	.154	.00358
Density of solution		0.872	5	122	.253	.00394
Molality (per 1000 g. of			6	122	.246	.00378
solution)		1.000	7	168	.337	.00428
Moles of solvent		16.65	8	168	.334	.00423
Normality		0.706	9	216	.404	.00444
Weight of sample analyzed			10	216	.405	.00446
(average of 3)		2.864 g.				

Calculations

Average point from 1 to 6	$t_1 = 72.7$	$K_1 = 0.00361$
Average point from 5 to 10	$t_2 = 126.7$	$K_2 = 0.00419$
	$t = 96.0$	$K = 0.00058$
Whence 0.00361 − 0.00000605 × 72.7 =		$K = 0.00318$

In Table III are given the results of the several experiments. In the first column are the numbers of the experiments. In the second the solvents used are listed. In the third, values of the density of the solvent used and the best recorded density are given. In the case of benzene, for example, the figures $^{22}/_{36}$ signify that the density of the benzene used was 0.8722, whereas the most probable figure for the true density is 0.8736. In the fourth column (M) are given the molalities of the solutions expressed as moles of each solute per 1000 g. of the solvent. In the fifth column

(*N*) the normality is expressed as moles per 1000 cc. of solvent. In the sixth and seventh columns are the values of the velocity constants found.

Table III

Second Order Velocity Constants of the Reaction between Pyridine and Ethyl Iodide in the Solvents Listed

Temperature, 25.00°. Time in hours

No.	Solvent	Density	*M*	*N*	*K*	Average *K*
1	Acetone	65/54	0.500	0.368	0.0387	0.039
2	Acetone	65/54	.500	.368	.0385	
3	Acetone	55/54	1.000	.695	.0352	.036
4	Acetone	55/54	1.000	.695	.0366	
5	Nitrobenzene	78/81	0.200	.231	.0691	.069
6	Nitrobenzene	78/81	.201	.232	.0694	
7	Nitrobenzene	78/81	1.002	1.004	.071	.071
8	Nitrobenzene	78/81	1.007	1.009	.070	
9	Benzene	22/36	0.500	0.404	.00250	.0028
10	Benzene	22/36	1.000	.769	.00277	
11	Benzene	22/36	1.004	.767	.00286	
12	Benzene	36/36	1.000	.767	.00292	
13	Methyl alcohol	76/67	1.000	.699	.00687	.0070
14	Methyl alcohol	76/67	1.000	.699	.00718	
15	Ethyl alcohol	51/51	1.000	.695	.00385	.0039
16	Ethyl alcohol	51/51	1.000	.695	.00387	
17	*n*-Propyl alcohol	98/98	1.000	.706	.00318	.0031
18	*n*-Propyl alcohol	98/98	1.000	.706	.00304	
19	*Iso*propyl alcohol	11/08	1.000	.690	.00313	.0030
20	*Iso*propyl alcohol	11/08	1.002	.691	.00296	
21	*n*-Butyl alcohol	58/57	1.004	.717	.00295	.0031
22	*n*-Butyl alcohol	58/57	1.009	.718	.00318	
23	*Sec.*-butyl alcohol	25/23	1.000	.706	.00275	.0028
24	*Sec.*-butyl alcohol	25/23	1.11	.706	.00285	
25	*Tert.*-butyl alcohol	07/06	1.000	.688	.00258	.0026
26	*Tert.*-butyl alcohol	07/06	1.002	.689	.00272	

In experiments numbered 1 and 2 a sample of acetone containing a trace of water was used. The constant is higher than that obtained in 3 and 4. Menschutkin found in his experiments that the presence of 8% of water in acetone increased the velocity constant about 46%.

The values obtained in Expts. 5, 6, 7 and 8 indicate that the effect on the constant of a change in concentration of the reactants is slight. From Expts. 11 and 12 it is seen that a sample of benzene having the density 0.8722 gave the same result as a sample with true density, 0.8736.

Since a knowledge of the purity of the substances used in the determination of velocity constants is of paramount importance, a brief account will be given of the methods employed in this research. The determinations of boiling points were made with thermometers which were checked against standards from the Reichsanstalt of Berlin. Fractional distillations were carried out with efficient columns. Densities were determined with a Sprengel pycnometer, capacity about 13 cc., provided with ground glass caps. A counterpoise was used and the weighings were reduced to vacuum.

Pyridine.—Eastman's White Label pyridine was converted into the ferrocyanide, which was washed with a mixture of water and ether containing enough alcohol to make a homogeneous liquid. Pyridine was liberated by potassium hydroxide and taken up in ether. The latter was removed by boiling, the residue dried over quick lime and fractionated. A fraction was obtained, 90% of which on redistillation boiled within 0.2° around 115.3°. The densities of the material used varied between 0.97753 and 0.97764 at 25°/4°.

Ethyl Iodide.—Eastman's White Label ethyl iodide was shaken with cold sulfuric acid (3 vols. C. P. concd. H_2SO_4 and 1 vol. H_2O), separated and distilled from a flask containing silver powder and a few small lumps of marble, after preliminary heating for an hour at 60°. The distillation was carried out in an atmosphere of carbon dioxide. A fraction was obtained, 95% of which boiled on redistillation within 0.1° around 72.3°. The material was kept in the dark in a bottle containing carbon dioxide It remained colorless for a long time. The density of the samples prepared varied between 1.9234 and 1.9241 at 25°/4°.

Acetone.—Eastman's White Label acetone from the bisulfite compound was distilled from potassium permanganate. The process was repeated until a sample was obtained which did not give a precipitate with the permanganate after standing for twenty-five hours. The acetone was distilled off and allowed to stand with a small amount of C. P. anhydrous potassium carbonate. When there was no evidence of any action the acetone was distilled. A fraction was obtained that boiled on redistillation almost completely within 0.1° around 56.1°. The density of the sample was 0.7855 at 25°/4°.

Benzene.—A high grade sample of "reagent quality" benzene was purified by the method described by Richards.[5] The product melted sharply at 5.42°. Its density was 0.8736 at 25°/4°.

Nitrobenzene.—Eastman's Blue Label nitrobenzene was distilled under diminished pressure. The product was alternately partially melted and the liquid poured off. This process was repeated until a small amount was obtained which gave good melting and freezing curves; m. p. 5.75°; density, 1.1978 at 25°/4°.

The Alcohols.—The alcohols were purified in general by the procedures used in this Laboratory in previous investigations. The values for the densities obtained at 25°/4° were as follows: methyl, 0.7866; ethyl from 0.78507 to 0.78511; propyl, 0.78998; *iso*propyl, 0.7811; *n*-butyl, 0.8058; *sec.*-butyl, 0.8025; *tert.*-butyl, 0.7807 (m. p. 24.5°).

Summary

1. It is pointed out that the results of the determination of the velocity constants of reactions in which an alcohol serves simultaneously as a reactant and as a solvent cannot be correctly interpreted without a knowledge of the effect of the solvent on the rate at which the reaction takes place.
2. *Adjuvance* is suggested as a convenient word to be used in expressing the property possessed by liquids of affecting the rate at which reactions proceed when the liquids are present as solvents.
3. The velocity constants of the reaction between pyridine and ethyl

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[5] Richards and Shipley, THIS JOURNAL, **36**, 1825 (1914).

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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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).