

The Reaction Rates of Propionic and Acetic Propionic Anhydrides

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Citation: [The Journal of Chemical Physics](#) **4**, 90 (1936); doi: 10.1063/1.1749806

View online: <http://dx.doi.org/10.1063/1.1749806>

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troscopic data do not strongly indicate the correctness of any particular geometrical configuration.

Comparison of the Raman spectra of the room temperature and high temperature forms of NH_4Cl suggests various possibilities. Of these, the simplest are that the frequencies occurring at room temperature at 2010 and 1768 cm^{-1} originate in similar types of vibration and that the

properties of NH_4^+ undergo only minor changes at the high temperature transition point.

The author is indebted to the physics departments at Lehigh University and the University of Virginia for laboratory facilities, and wishes to thank Dr. J. E. Rosenthal of Columbia University for discussions, and Professor W. W. Watson of Yale University for his interest and advice.

FEBRUARY, 1936

JOURNAL OF CHEMICAL PHYSICS

VOLUME 4

The Reaction Rates of Propionic and Acetic Propionic Anhydrides

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(Received October 4, 1935)

The infrared absorption spectra of mixtures of water and acetic propionic and of propionic anhydrides have been measured in the region from 5μ to 6.4μ . The intensity of the bands was found to decrease with time. By using the relative intensity of the anhydride band the reaction rate was calculated for three concentrations. The reactions were unimolecular but the value of the reaction constant

was different for each concentration, its value being approximately proportional to the concentration of the water. The value of the reaction constant of acetic propionic anhydride was about twice the value of the constant for propionic anhydride. A table is given of the values of the reaction constants for the different concentrations.

THE reaction velocity of acetic anhydride has been measured¹ recently by means of its infrared absorption spectra. The results showed that the reaction constant increased with temperature and that the value of the constant decreased in a given set of observations. The latter result may have been produced by the method of calculation. In order to study further the effect of concentration the work has been extended to propionic and acetic propionic anhydrides. Before the absorption spectra of different concentrations were measured the region from 5μ to 6.5μ was studied. It was found that the absorption spectra of acetic and of propionic acid were similar in this region and that the bands, which were at about 5.7μ , varied in position by about 0.03μ . The propionic and acetic propionic anhydrides were studied and it was found that there were two absorption bands at 5.48μ and 5.66μ , and 5.50μ and 5.68μ , respectively. When cells of about 0.01 mm in thickness were used, the two bands could be separated by the fluorite

prism. The two anhydrides have similar spectra, as can be seen by the absorption curves shown in Fig. 1. The fact that the 5.50μ band can be separated from the other anhydride band at 5.68μ and the acid bands at 5.7μ made it suitable for the study of reaction rates.

In the study of the reaction velocity, cells were made of three concentrations. The first solution had equivalent amounts of water and anhydride, the second two equivalent parts of water to one of anhydride, and the third three of water and one of anhydride. The actual concentrations of water and anhydride are given in Table I. The same concentrations were used for each anhydride. The reactions were allowed to progress in the absorption cell. After preliminary trials it was found that the reactions were slow and that the absorption curves should be measured at time intervals of from one to two hours. In this way six to eight sets of observations were obtained for each concentration. In Fig. 2 are shown the curves for the three concentrations of propionic anhydride. The bands in the section on the left are for equivalent amounts and the time of observation

¹ Plyler and Barr, J. Chem. Phys. 3, 679 (1935).

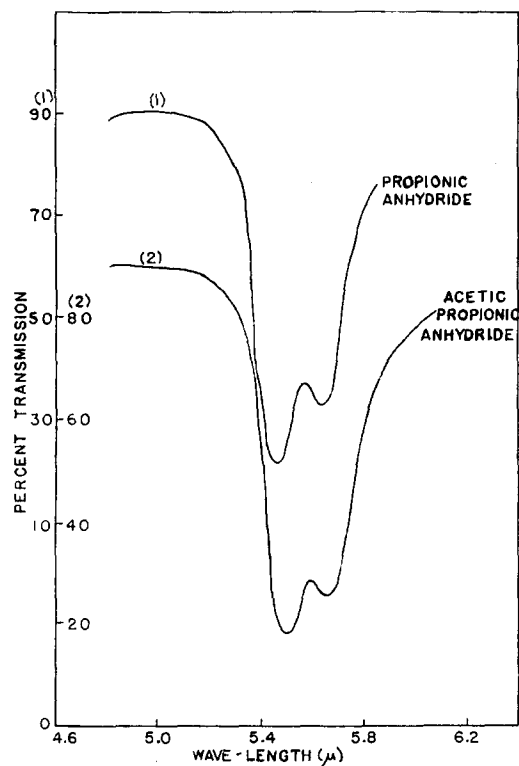


FIG. 1. The absorption spectra of propionic and acetic propionic anhydrides in the region from 4.8μ to 6.1μ . The cell thickness was 0.01 mm.

is given beside each curve. The fourth curve in the first group was placed inaccurately on the drawing. It should be shifted 0.06μ to the shorter wave-lengths. The middle set of observations are for two parts water and one part anhydride. The lowest curve in each set is for the shortest interval of time after mixing, and shows the 5.48μ band with the greatest intensity. These curves show that in any concentration the absorption in the region of 5.5μ decreases with time. Also this decrease in intensity with time is greater when the concentration of the anhydride is smaller. Three sets of observations were also made for the acetic propionic anhydride. The absorption spectra were similar to those shown in Fig. 2.

It was found by considering the reaction as unimolecular, that approximately consistent values were obtained for the reaction constant. In order to find the concentration of the anhydride at any time, it was necessary to know the relative intensity of the band at the beginning of the reaction and also the relative intensity at the time of

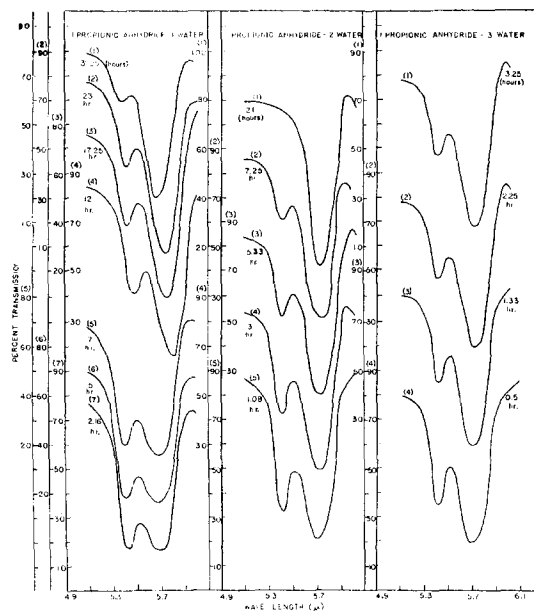


FIG. 2. The absorption of propionic anhydride and water after different intervals of time. The different sets of curves represent mixtures of 1, 2 and 3 parts water to one part anhydride.

TABLE I. The reaction constants of propionic and acetic propionic anhydrides at 27°C , for different concentrations.

SUBSTANCE	CONCENTRATION (mole/l)		TIME (sec.)	$k \times 10^4$
	H ₂ O	ANHYDRIDE		
Propionic anhydride	6.85	6.85	7800	0.32
			18000	0.26
			25200	0.27
			43200	0.25
	12.2	6.1	3900	0.52
			10800	0.47
			19200	0.41
			26100	0.41
	16.5	5.5	1800	1.6
			4800	1.1
			8100	1.0
			11700	1.0
Acetic propionic anhydride	7.65	7.65	6600	0.67
			10800	0.65
			16200	0.65
			23400	0.53
			30600	0.45
	13.58	6.74	2400	1.3
			4500	1.1
			7200	1.0
			9900	0.95
			13800	1.1
			17400	1.1
	18.00	6.00	1800	3.0
			3600	2.7
			5400	3.0
			7200	2.8

the observation. The relative intensity of the bands for different times of observation was found by determining the area under the absorption curve. The relative intensity at zero time was found by extrapolation.²

In Table I the values of the reaction constant are given for the reaction rate of propionic and acetic propionic anhydrides.

The constant for acetic propionic anhydride is roughly twice that of propionic anhydride for each concentration. For a given concentration the values of k tend to decrease with time. However, this effect is not so great as found in the case of acetic anhydride. The change in the value

² A more complete description of the method of calculation can be found in the paper of reference 1.

of the constant may not be a real property of the reaction. The method of measurement and calculation may produce the change. All measurements were made at 27°C.

When the concentration of water in the solution was increased the reaction rate increased. It was found that the value of k for the different concentrations was approximately proportional to the equivalent amounts of water in the mixture.

On account of the anhydride band being less overlapped by the acid band, it is believed that the accuracy is greater than in the previous study of acetic anhydride. The percent error in the results are probably between 5 and 10 percent.

The Near Infrared Absorption Spectra of Acid and Basic Solutions

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The infrared absorption spectra of H_2O and aqueous solutions of HCl , HBr , $NaOH$, KOH , $ZnBr_2$, $ZnCl_2$ and Na_2CO_3 have been measured from 1.5μ to 2.8μ . Bands were observed at 2.30μ and 2.45μ in hydroxides, at 2.30μ and 2.55μ in acids, and at 2.30μ , 2.45μ and 2.55μ in hydrolyzing salts. The band at 2.30μ is produced by hydration and 2.45μ band by the OH ion.

STUDIES¹ have already been made on the infrared absorption of acid and basic solutions from 1μ to 7μ . In the study on acid solutions a broad band was observed at 2.4μ and in the hydroxide solutions at 2.3μ . When the hydrolyzing salts were studied, the two bands could not be separated. With greater resolution it would be possible to separate the bands in the 2.4μ region.

A large type Hilger infrared spectrometer, with a quartz prism, was used for the resolving instrument. The deflections were increased by using a Moll thermorelay. The effective slit width at 2.5μ was 0.015μ . The percent absorption of water was first determined in order that a comparison could be made with the absorption curves of the solu-

tions, the thickness of all cells being 0.1 mm. The absorption spectra for some of the solutions which were studied are shown in Fig. 1. It can be seen that the absorption of all the solutions in the region of 2.4μ is greater than that of water. Aqueous solutions of KOH , $NaOH$, $ZnBr_2$, and $ZnCl_2$ of 5 and 10 N concentrations, 5 N Na_2CO_3 , 18 and 36 percent HCl , and 17 and 34 percent HBr were studied. The ratio of the percent absorption of the solutions to that of water was plotted and the results are shown in Fig. 2. The water content of the solution cells was less than in the water cell and the transmission is greater than 100 percent at some wave-lengths. Also, because of the shift of the 1.95μ water band to longer wave-lengths in some of the solutions, a minimum appears at about 2μ , but this is not an actual band.

¹ E. K. Plyler and E. S. Barr, *J. Chem. Phys.* **2**, 306 (1934); E. K. Plyler and W. Gordy, *J. Chem. Phys.* **2**, 470 (1934).