

The marked rise in decomposition at 2537 Å. cannot be due to activation of mercury vapor in the absorption tube, for spectrum photographs show that with the type of high pressure arc used in this study the 2537 Å. resonance line is completely reversed, only the wings and the continuum to the long wave length side, which are not absorbed by cold mercury vapor, being present.

The authors wish to acknowledge their indebtedness to Dr. J. H. C. Smith for many helpful suggestions made during the course of this work.

Summary

1. The first of a series of articles on the photochemical reactions of the aliphatic aldehydes has been presented. The apparatus and method of study has been described and the experimental results given for propionaldehyde.

2. In the region investigated, λ 2537 Å. to λ 3130 Å., photochemical decomposition and polymerization are independent reactions. The quantum yield of decomposition is independent of pressure, while the quantum yield of apparent polymerization is directly proportional to the pressure.

3. The variation of the quantum yields of both reactions with wave length has been studied.

4. The principal products of decomposition were found to be carbon monoxide and ethane. A small amount of hydrogen also was formed in decomposition.

5. Fluorescence was produced by exposure to all wave lengths down to and including λ 2654 Å.

6. Mechanisms for both photochemical reactions have been proposed.

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[CONTRIBUTION FROM THE ANATOMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

DISTRIBUTION OF ACIDS BETWEEN WATER AND SEVERAL IMMISCIBLE SOLVENTS

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Part I. Monocarboxylic Acids

The distribution ratios at 25° of the six straight-chain members of the saturated monocarboxylic acid series from formic acid to caproic acid have been determined between water and the following solvents: ethyl methyl ketone, tertiary amyl alcohol, secondary butyl alcohol, normal butyl alcohol and normal amyl alcohol. Data have also been included from the literature for ratios between ethyl ether and water¹ and between isopropyl

¹ W. U. Behrens, *Z. anal. Chem.*, **69**, 97 (1926).

ether and water.² Since the distribution ratios change slightly with the concentration of the acid, the values of the ratios for ethyl ether have been estimated for an acid concentration of about 0.001 *M* in the water layer. The values for isopropyl ether and water were obtained by using weighted means from the three papers cited for an average acid concentration of both layers of about 0.05 *M*. These values of the distribution ratios in water and ethyl ether, and in water and isopropyl ether are included in the table and plot of the original data. The exact concentrations in the ether layers cannot be calculated because the volumes after mixing are not given. Note: The value given for butyric acid by Werkman in his first paper is undoubtedly in error.

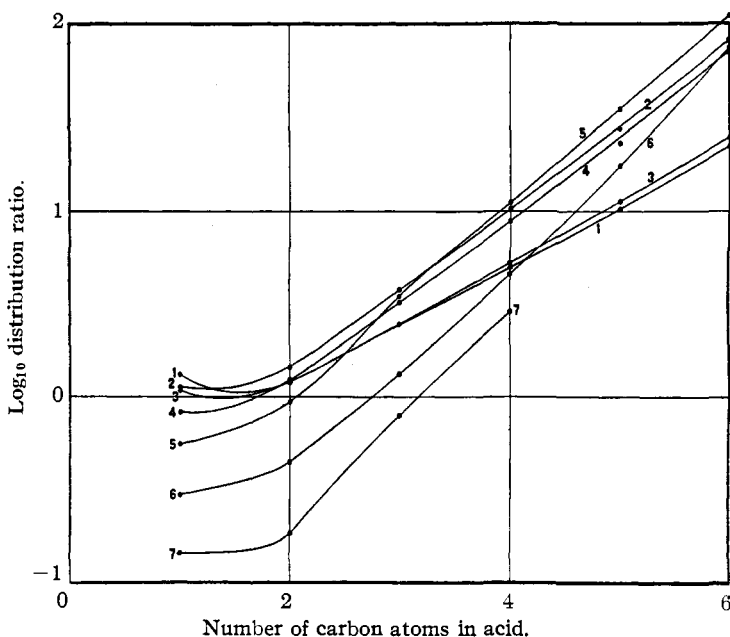


Fig. 1.—Distribution of monocarboxylic acids: 1, ethyl methyl ketone; 2, tertiary amyl alcohol; 3, secondary butyl alcohol; 4, normal butyl alcohol; 5, normal amyl alcohol; 6, ethyl ether; 7, isopropyl ether. Ratios are: moles per liter in solvent layer/moles per liter in water layer.

The plot, Fig. 1, shows the logarithm of the distribution ratio at the concentration given in Table I, or in cases where two concentrations are given, the logarithm of the average distribution ratio.

Experimental

Industrial solvents were obtained from Shell Chemical Company, Sharples Solvents Corporation, Commercial Solvents Corporation, Carbide

² C. H. Werkman, *Ind. Eng. Chem., Anal. Ed.*, **2**, 302 (1930); O. L. Osburn and C. H. Werkman, *ibid.*, **3**, 264 (1931); C. H. Werkman and O. L. Osburn, *ibid.*, **3**, 387 (1931).

and Carbon Chemicals Corporation, etc. Some were first washed with 20 normal aqueous sodium hydroxide and all were of the highest purity, having been distilled in a 20-foot (6.09 m.) fractionating column described

TABLE I
DISTRIBUTION RATIOS OF MONOCARBOXYLIC ACIDS
 Concentrations in millimoles per liter

Acid	Concn. H ₂ O layer	Concn. solv. layer	Ratio	Av. ratio
Ethyl Methyl Ketone and Water				
Formic	122.69	165.11	1.3457	1.320
Formic	342.52	443.32	1.2942	
Acetic	148.26	178.66	1.2050	1.193
Acetic	460.45	543.51	1.1804	
Propionic	76.45	189.50	2.4787	2.4787
Butyric	32.78	166.44	5.0774	5.045
Butyric	122.88	615.99	5.0129	
Valeric	31.57	322.36	10.211	10.211
Caproic	13.43	298.89	22.260	22.260
Tertiary Amyl Alcohol and Water				
Formic	114.43	130.15	1.1373	1.119
Formic	360.56	397.05	1.1012	
Acetic	132.05	195.31	1.4791	1.445
Acetic	374.27	528.29	1.4115	
Propionic	52.01	198.29	3.8125	3.8125
Butyric	16.01	166.97	10.367	10.29
Butyric	52.32	535.05	10.226	
Valeric	11.97	330.74	27.631	27.631
Caproic	3.55	291.72	82.17	82.17
Secondary Butyl Alcohol and Water				
Formic	118.30	127.81	1.0804	1.074
Formic	346.25	369.53	1.0672	
Acetic	151.00	192.12	1.2723	1.206
Acetic	466.70	531.82	1.1395	
Propionic	72.21	178.46	2.4714	2.4714
Butyric	31.25	159.63	5.1082	5.289
Butyric	91.22	498.96	5.4699	
Valeric	27.42	311.39	11.356	11.356
Caproic	11.65	288.61	24.773	24.773
Normal Butyl Alcohol and Water				
Formic	256.22	225.07	0.8486	0.829
Formic	784.93	635.54	.8097	
Acetic	150.72	187.57	1.2445	1.232
Acetic	420.54	513.07	1.2200	
Propionic	57.62	186.20	3.2315	3.2315
Butyric	21.09	187.61	8.8957	8.814
Butyric	57.66	503.50	8.7322	
Valeric	13.71	315.50	23.012	23.01
Caproic	4.03	287.40	71.32	71.3

TABLE I (Concluded)

Acid	Concn. H ₂ O layer	Concn. solv. layer	Ratio	Av. ratio
Normal Amyl Alcohol and Water				
Formic	143.86	83.18	0.5782	0.549
Formic	489.89	254.72	.5200	
Acetic	164.51	153.05	.9303	.935
Acetic	488.28	458.64	.9393	
Propionic	53.34	186.00	3.4871	3.4871
Butyric	15.52	173.38	11.171	11.15
Butyric	46.67	519.12	11.123	
Valeric	8.83	312.88	35.43	35.43
Caproic	2.60	284.26	109.3	109.3
Ethyl Ether and Water				
Formic			0.30	
Acetic			.44	
Propionic			1.34	(Cf. Ref. 1)
Butyric			4.6	
Valeric			17.5	
Caproic			75	
Isopropyl Ether and Water				
Formic			0.145	
Acetic			.184	
Propionic			.810	(Cf. Ref. 2)
Butyric			2.90	

elsewhere.³ Blank titrations were made on all solvents in equilibrium with distilled water at 25°. These titrations showed no appreciable acid in either the water or any of the solvents. The acids used were high grade commercial c. p. products.

The solvent, water and acid were mixed in a flask and allowed to remain, with frequent shaking, in a thermostat at 25.00 ± .01° for several hours. Samples of each layer were pipetted out and titrated in duplicate against standardized 0.1 *N* sodium hydroxide with phenolphthalein indicator. These samples were 25 cc. in all cases except the higher concentrations of formic, acetic and butyric acids, for which 10-cc. samples were used. The values in Table I were obtained from the average of the duplicate titrations. The close check of the duplicate titrations showed that equilibrium had been attained.

Discussion

This work was undertaken for its bearing on the possibility of separating sterols from vitamins by forming some ester of the sterol, such as the gluconate, which might be slightly soluble in water, and fractionating the mixture in a column which gives multiple distribution between two immiscible solvents. The construction and use of this column will be pub-

³ Evans, Cornish, Lepkovsky, Archibald and Feskov, *Ind. Eng. Chem., Anal. Ed.*, 2, 339 (1930).

lished later in a paper from this Laboratory dealing with the isolation of the fat-soluble vitamins.

This work is also of interest in connection with the Dakin process for separating amino acids.⁴ This process consists in extracting a water solution of the mixed amino acids with normal butyl alcohol or other solvent. The strongly ionized amino acids remain in the water layer, while the slightly ionized acids are extracted. A similar process is also being used in this Laboratory in an attempt to isolate some of the water-soluble vitamins.

Part II. Inorganic Acids

This part of the paper will consider the distribution of hydrochloric, nitric, sulfuric and perchloric acid between water and some of the non-

TABLE II
DISTRIBUTION OF INORGANIC ACIDS

Concentrations in equivalents per liter, except aniline values, which are moles per 1000 g. of solution.

Acid	Concn. solv. layer	Concn. H ₂ O layer	Acid	Concn. solv. layer	Concn. H ₂ O layer
Solvent: <i>n</i> -Butyl Alcohol			Solvent: Methyl Ethyl Ketone		
HCl	0.0105	0.0839	HCl	0.0024	0.0695
HCl	.0857	.4197	HCl	.0117	.3438
HCl	.7586	1.7973	HCl	.1497	1.3749
HNO ₃	.0208	0.0856	HNO ₃	.0088	0.0647
HNO ₃	.1455	.3657	HNO ₃	.0935	.2871
HNO ₃	.9841	1.5481	HNO ₃	Miscible	
H ₂ SO ₄	.0056	0.0937	Solvent: Ethyl Ether		
H ₂ SO ₄	.0387	.4745	HNO ₃	0.0011	0.0847
H ₂ SO ₄	.3412	2.3416	HNO ₃	.0165	.4326
HClO ₄	.0353	0.0774	HNO ₃	.4263	1.9071
HClO ₄	.2088	.3224	Solvent: Aniline (Cf. Ref. 5)		
HClO ₄	1.1271	1.4065	HCl	0.00599	0.1110
Solvent: <i>n</i> -Amyl Alcohol			HCl	.01939	.2039
HCl	0.0026	0.0929	HCl	.04190	.2892
HCl	.0279	.4836	HCl	.04886	.3117
HCl	.4213	2.1964	HCl	.05758	.3361
HNO ₃	.0071	0.0974	HCl	.09151	.4240
HNO ₃	.0829	.4794	HCl	.1134	.4594
HNO ₃	.7021	1.8708	HCl	.1816	.5514
H ₂ SO ₄	.0018	0.1007	HCl	.3371	.7126
H ₂ SO ₄	.0059	.5052	HCl	.8558	1.0247
H ₂ SO ₄	.0787	2.4714	HCl	1.1299	1.1622
Solvent: <i>Tert</i> -amyl Alcohol			HCl	1.1876	1.1832
HCl	0.0109	0.0956	HCl	1.446	1.3320
HCl	.1010	0.4385	HCl	1.578	1.578
HCl	.9616	1.7882			
H ₂ SO ₄	.0056	0.0984			
H ₂ SO ₄	.0464	.4923			
H ₂ SO ₄	.4969	2.2337			

⁴ H. Dakin, *Biochem. J.*, 12, 290 (1918).

aqueous solvents used in Part I. Distributions of these acids were determined in three concentrations, the average concentration for both layers being about 0.05, 0.25 and 1.25 *N*. The layers were approximately equal in volume.

The experimental method is identical with that used for the monocarboxylic acids; 25-cc. samples were used in the two lower concentrations and 10-cc. samples in the highest.

The data on hydrochloric acid in aniline are due to Sidgwick, Pickford and Wilsdon.⁵

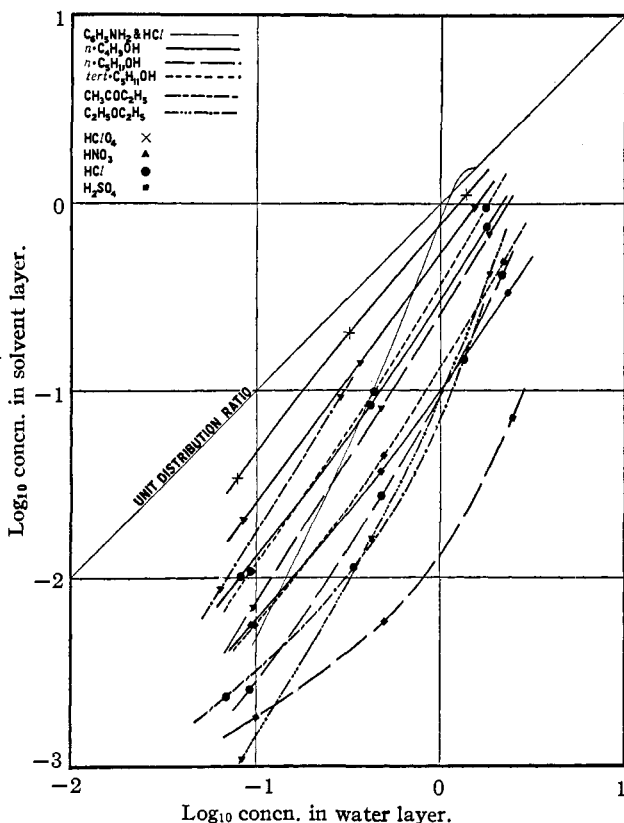


Fig. 2.—Distribution of inorganic acids. Concentrations are in equivalents per liter, except aniline values where hydrochloric acid is in moles per 1000 g. of solution.

Table II shows the acid concentration in the water layer, and in the solvent layer in equilibrium with it. All measurements are at $25.00 \pm .01^\circ$.

In Fig. 2 the logarithm of the acid concentration in the aqueous layer is plotted against the logarithm of the acid concentration in the solvent layer.

⁵ N. V. Sidgwick, P. Pickford and B. H. Wilsdon, *J. Chem. Soc.*, 99, 1122 (1911).

Discussion

The tendency is for the curves to approach the line denoting unit distribution ratio as the acid concentration is increased. They reach this line at the point where complete miscibility between the two layers occurs, which in the case of nitric acid in ethyl methyl ketone and water is within the range of concentrations studied. The curves may cross this line before the point of complete miscibility, returning to it later, as in the case of aniline and hydrochloric acid.

The curve for hydrochloric acid in aniline and water has a slope of about 2 over most of its length. That is, the concentration of the hydrochloric acid in the aniline layer varies approximately as the square of the acid concentration in the water layer. From this fact it may be assumed that the hydrochloric acid is practically un-ionized in the aniline layer. This condition is approximated also in the curve representing nitric acid in ethyl ether and water. The other curves, however, apparently show more tendency for the acids to be ionized in the non-aqueous layers.

Distribution measurements were also attempted for hydrochloric acid between ethyl ether and water. However, due to the extreme insolubility of hydrochloric acid in ether at all the concentrations studied, it was impossible to make any accurate measurements without a much more refined procedure.

In any one solvent the order of the curves from the line of unit distribution ratio is HClO_4 , HNO_3 , HCl , H_2SO_4 , which follows the Hofmeister series for the precipitation of proteins, the sulfate ion being the most efficient. The series is also the same as that found by Randall and Failey⁶ for the salting-out effect, rather than the strength of acids series⁷ which gives the order HNO_3 , HCl , H_2SO_4 , HClO_4 , where perchloric is the strongest acid.

An attempt was made to measure the distribution of hydrochloric acid between propylene oxide and water, but due to the rapid reaction of propylene oxide with hydrochloric acid⁸ even in cold dilute aqueous solution, these measurements were impossible. Propylene oxide is more reactive than propylene glycol and consequently much more reactive than ethers such as ethyl ether. This extreme reactivity is probably due to the fact that the oxygen atom is one member of a three-membered ring, and this makes propylene oxide more suitable as a reagent than a solvent.

The purpose of this research was to determine quantitatively which acid would be most suitable for acidifying a water solution, one component of

⁶ Randall and Failey, *Chem. Rev.*, **4**, 285 (1927); *ibid.*, **4**, 271 (1927); *ibid.*, **4**, 291 (1927).

⁷ Hantzsch and Voigt, *Ber.*, **62B**, 975-984 (1929); Hantzsch and Langbein, *Z. anorg. allgem. Chem.*, **204**, 193 (1932); Hall, *The Nucleus*, **6**, 87-88, 91 (1929).

⁸ Henry, *Bull. acad. roy. Belg.*, p. 397 (1903); Michael, *Ber.*, **39**, 2786 (1906); Smith, *Z. physik. Chem.*, **93**, 59 (1919); Markownikoff, *Compt. rend.*, **81**, 799 (1875); Nef, *Ann.* **335**, 205 (1904).

which was to be extracted out with one of the solvents mentioned above. Since it was necessary to extract with very large amounts of solvent, many times it was imperative that the acid be very insoluble in the solvent in order that the solution remain acid until the end of the extraction process.

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Summary

Distribution ratios of six fatty acids and four inorganic acids were measured between water and several solvents which are not miscible with water. A short discussion of the results is given.

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[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

THE KINETICS OF GAS EXPLOSIONS. III. THE INFLUENCE OF HYDROGEN ON THE THERMAL DECOMPOSITION OF OZONE SENSITIZED BY BROMINE VAPOR, AND THE DE-TERMINATION OF THE EXPLOSION TEMPERATURE¹

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In a previous paper⁴ it was shown that inert gases exert a small influence on the rate of decomposition of ozone in the presence of bromine as long as the ozone pressure is low. At higher pressures the rate is slowed down and the explosion pressure limit of ozone is increased considerably. The efficiency of inert gases in increasing the explosion limit decreases with increasing molecular weight.

The influence of hydrogen was not included in the previous investigations. It seemed of special interest, as hydrogen increases considerably the photochemical rate of decomposition of ozone with the simultaneous formation of water.⁵ Belton, Griffith and McKeown⁶ found a similar influence of hydrogen on the thermal decomposition of ozone, whereas Schumacher⁷ states that hydrogen has only a slight effect on the thermal

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⁴ Part I, *THIS JOURNAL*, **53**, 2910 (1931). Part II, *ibid.*, **54**, 1784 (1932).

⁵ Weigert and Böhm, *Z. physik. Chem.*, **90**, 189 (1915); Griffith and Shutt, *J. Chem. Soc.*, **123**, 2752 (1923).

⁶ Belton, Griffith and McKeown, *ibid.*, **126**, 3153 (1926).

⁷ Schumacher, *THIS JOURNAL*, **52**, 2388 (1930).