

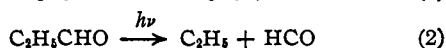
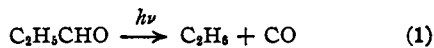
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

Free Radicals in the Photolysis of Propionaldehyde*

BY LEONARD MAY, H. AUSTIN TAYLOR AND MILTON BURTON

There is much evidence, of an indirect nature, that both the pyrolysis¹ and the photolysis² of propionaldehyde proceed *via* a free radical mechanism. This view of the data has been examined theoretically³; the conclusions arrived at indicate that in this respect propionaldehyde behaves like the other aldehydes. However, when attempts were made to detect free radicals in the photolysis of propionaldehyde by the para-ortho hydrogen conversion method⁴ and by the Paneth mirror method,⁵ the results were negative. The results with the former method are not inexplicable, for it is known that the para-ortho conversion occurs only when the particles effecting the conversion do not enter into other reactions more readily.⁶ In regard to the mirror method, Pearson and Purcell⁷ subsequently showed that similar negative results obtained with acetaldehyde were attributable to interference by a polymer formed in the course of the photolysis and that such interference can be eliminated by suitable precautions (*e. g.*, heating the mirror gently during the run).

In view of the theoretical importance of the questions involved in the cases of compounds which may decompose by competing mechanisms,⁸



in this case it was deemed advisable to repeat the Paneth mirror investigation of the photolysis of propionaldehyde, using improved techniques where possible.

Experimental

The technique employed in this investigation was, with little modification, similar to that used in studies of

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(1) L. A. K. Staveley and C. N. Hinshelwood, *J. Chem. Soc.*, 812 (1936).

(2) P. A. Leighton and F. E. Blacet, *THIS JOURNAL*, **54**, 3165 (1932).

(3) (a) M. Burton and G. K. Rollefson, *J. Chem. Phys.*, **6**, 416 (1938); (b) H. A. Taylor and M. Burton, *ibid.*, **7**, 414 (1939).

(4) W. West, *THIS JOURNAL*, **57**, 1931 (1935).

(5) T. G. Pearson, *J. Chem. Soc.*, 1718 (1934).

(6) Cf. G. K. Rollefson and M. Burton, "Photochemistry and the Mechanism of Chemical Reactions," Prentice-Hall, Inc., New York, N. Y., 1939, p. 117.

(7) T. G. Pearson and R. H. Purcell, *J. Chem. Soc.*, 1151 (1935).

(8) Cf. P. A. Leighton, "The Determination of the Mechanism of Photochemical Reactions," Hermann et Cie., Paris, 1938; G. K. Rollefson and M. Burton, *J. Chem. Phys.*, **6**, 674 (1938).

the photolysis of fatty acids.⁹ Figure 1 is a schematic diagram of the set-up. A, B, C, and D represent the vacuum purification system, with the final reservoirs C for propionaldehyde and D for acetone. Pressure of the flowing vapors was controlled by stopcock 6 and measured by means of sloping manometer F, which had a slope of 24.2:1. The wide portion of the tube at G contained silver turnings to prevent passage of mercury vapor through the stopcock 7. The quartz tube J was 5.22 mm. in internal diameter, and the effective constricted length between G and E, allowing for stopcocks and bends, was fixed at 82.5 cm. Terminal trap E, cooled with liquid nitrogen, was used to recover propionaldehyde and acetone for use in subsequent experiments. Glass steam jacket H, used over the lead mirrors,⁷ was 15 cm. long, sufficient to cover both test and guard mirrors, and was movable.

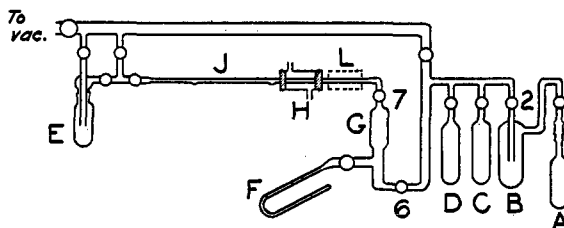


Fig. 1.—Set-up of apparatus for mirror experiments.

Light Source.—In most of this work the lamp used was a quartz-spiral low-pressure 5000 volt mercury arc, L, supplied by Hanovia. The inside diameter of the tubing was 5 mm. The inside diameter of the spiral was 3.5 cm. and its axial length 11 cm. There were nine turns in the spiral.¹⁰ The lamp was fixed alongside the quartz tube at a distance of 2 mm. and illuminated the zone 5–20 cm. from the beginning of the constricted region; the illuminated zone was delimited by copper shields and a shutter. The temperature of the arc was held constant at 55° by air cooling, while that of the irradiated zone did not rise above that value. In all the quantitative experiments the output of the lamp was controlled by a fixed, constant-current transformer, the current in the primary of which was held at 6.4 amperes by means of an Adjust-a-Volt transformer used to correct small fluctuations in the 110-volt supply line.

A vacuum of 10⁻⁶ mm. or better was established before each series of runs. Large stopcocks were used throughout, with the exception of those closing the reservoirs, and Lubri-seal grease was employed.

Chemicals.—Propionaldehyde was purified from the Eastman Kodak Co. product. Since this material readily oxidizes and polymerizes in the absence of a preservative, speed was necessary in all transfers of material. The middle fraction of the aldehyde was distilled into a ground-glass

(9) (a) M. Burton, *THIS JOURNAL*, **58**, 1645, 1655 (1936); (b) H. Henkin and M. Burton, *ibid.*, **60**, 831 (1938).

(10) This lamp is similar to one used by D. H. Etzler and G. K. Rollefson, *ibid.*, **61**, 800 (1939) (private communication).

stoppered flask containing Drierite and hydroquinone and allowed to stand for two days. The middle fraction of this product was then distilled into a clean glass vessel, and this preservative-free material was immediately redistilled (to obtain a true boiling point), with generous rejections, into a vessel containing a trace of hydroquinone. The corrected boiling point of the fraction taken was 47.8–48.0°. ¹¹ This fraction was stored overnight in trap A, with Drierite and hydroquinone, at 0°, in position in the apparatus, but not under vacuum. It was then cooled to dry-ice temperature and evacuated. Following a series of degassing operations, the propionaldehyde was distilled repeatedly from A to B, with stopcock 2 open, and from B to A with stopcock 2 closed. ¹² Finally it was distilled into and stored in C. Dry-ice was the only refrigerant used in this section of the apparatus. The last fraction of the first distillation *in vacuo* was rejected. The first and last fractions of the final distillation *in vacuo* were removed by appropriate means and found to be free from both acid and water.

Acetone from the best Eimer and Amend product was purified according to the method of Shipsey and Werner, ¹³ and fractionally distilled; the fraction used boiled in the corrected range 56.09–56.12° (*cf.* Pearson's figure of 56.1°). This fraction was degassed and distilled *in vacuo* in the same manner as propionaldehyde, except that no hydroquinone was used. The distillate was found to be free from both water and reducing agents before it was introduced into the apparatus.

Part I. Detection of Alkyl Radicals.—Standard lead mirrors were deposited as described by Pearson ⁵ by comparison with a smoked glass tube used as a primary standard. Guard mirrors were deposited as in the work on the fatty acids. ⁹ It was found that the products of the photolysis of acetone removed the lead mirrors readily ¹⁴ while the products of the photolysis of propionaldehyde had a similar effect only when the conditions of the experiment were very carefully controlled. In particular, it was found that propionaldehyde yields the last traces of oxygen only very slowly (necessitating the involved purification methods already described), and that a repeatedly used sample requires further degassing. Occasional recleaning of traps and greasing of stopcocks is also required. The technique for sensitizing the surface of the quartz tube prior to deposition

(11) The boiling point of propionaldehyde seems to be in dispute. Various hand-book values are 49.5° and 48.1–49.1° at 740 mm., and at 760 mm. Winkler, Fletcher and Hinshelwood, *Proc. Roy. Soc. (London)*, **146A**, 345 (1934), quote 48.5–49.5° as their middle fraction, while Pearson (*ref.* 5) observed 49.5°.

(12) A further degassing operation was performed on later samples by passing the propionaldehyde repeatedly through J with stopcock 10 open and reservoir E cooled in liquid nitrogen.

(13) K. Shipsey and E. A. Werner, *J. Chem. Soc.*, **103**, 1255 (1913).

(14) We found that quartz tubes intended for mirror work should not be cleaned with chromic acid. Mirrors deposited in tubes so prepared are entirely inactive. Nitric acid or aqua regia is satisfactory.

of the standard mirror is slightly different from the usual practice. ¹⁵ A light mirror is first deposited "upstream" from the point at which it is desired to deposit the standard mirror; it is then swept down the tube in the conventional manner ¹⁵ by means of free radicals produced by pyrolysis of propionaldehyde (upstream from the mirror). Only when the tube has been so prepared initially can a satisfactory mirror be put down in the usual way.

In the study of propionaldehyde photolysis with *lead* mirrors it is essential that the mirrors be warmed by a steam jacket; temperatures much above or much below 100° were found unfavorable. ² Although mirrors were readily, completely and repeatedly removed in a new quartz tube, traces of lead frequently remained in spite of precautions. Complete, clean-cut removal occurred in a sufficient number of cases, however, to indicate the reality of the result, but the actual times of removal varied so widely that no quantitative significance could be attached to them. In this respect, the results are to be contrasted with those in the acetone experiments, in which lead mirrors were removed completely both in the cold and at steam temperatures. The results with propionaldehyde are probably to be attributed to some kind of mirror desensitization, perhaps by polymer. ² We found in a number of experiments that when illuminated propionaldehyde vapors failed to remove a mirror, subsequent tests on the same mirror with illuminated acetone were similarly unsuccessful. This result had to be attributed to a desensitizing action of the propionaldehyde, for fresh mirrors deposited immediately after such experiments were readily removed by the products of acetone photolysis. Furthermore, we found that the time elapsed in the propionaldehyde experiments and prior to those with acetone could not of itself account for the desensitization of the mirrors, for mirrors treated with the products of acetone photolysis as much as two to three hours after deposition were readily removed, but in periods somewhat longer than usual.

It was concluded from these experiments that alkyl radicals actually were produced in the photolysis of pure propionaldehyde and that the earlier failure by others ⁵ to detect the radicals in this way was attributable to some kind of mirror desensitization in propionaldehyde. Because of

(15) F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935.

the extremely variable nature of this latter factor in the case of lead mirrors, quantitative (half-life) studies with such mirrors were not attempted.

Part II. Tests for Hydrogen Atoms.—The presence of atomic hydrogen in the presence of free alkyls was investigated through the guard mirror technique recently developed.⁹ Propionaldehyde was subjected to photolysis in each experiment until both the lead and antimony test mirrors disappeared, or until no propionaldehyde was left in the reservoir. Both the lead test and the lead guard mirrors were heated with steam. Similar experiments were conducted with acetone, a compound known not to produce hydrogen atoms, as a blank. It was found that the lead guard mirrors prevented the passage of free radicals in the case of acetone only when they were at least 35 mm. wide and the pressure of vapors was less than 2.6 mm. of Hg.¹⁶ Only experiments with wide freshly deposited guard mirrors were found satisfactory.

The results of guard mirror experiments with propionaldehyde conducted at 2.54 mm. pressure are shown in Table I. Only a fraction, f , of the antimony mirror was usually removed and the time of removal of a complete standard mirror, t_s , was calculated by dividing the actually observed time, t_{obs} , by f . If this attack on antimony mirrors is due to hydrogen atoms, the time of removal of a (hypothetical) properly guarded antimony mirror at the lamp exit, t_h , should be approximately 0.9 as great.^{9b} Since the extrapolated actual time of unguarded standard antimony mirror removal is 56 sec. (see Fig. 2), it is apparent that the maximum fraction of hydrogen atoms, f_H , among the mirror-active particles is $56 \div t_h$. If it is assumed that free hydrogen atoms are responsible for this antimony mirror removal, it is seen that they comprise less than 2% of the total number of mirror-active particles. On the other hand, if escaping alkyl radicals are the cause, a simple calculation based on the actually observed times of unguarded mirror removal, t_{sb} , at the corresponding distances, d , of the antimony mirrors from the lamp (see Fig. 2) gives the fraction of alkyl radicals which may be assumed to pass the guard mirror unaffected, f_{alk} . It is seen from

(16) F. Paneth and K. Herzfeld, *Z. Elektrochem.*, **37**, 577 (1931), state that a 10 mm. wide lead mirror is sufficient to prevent passage of 99.4% of the free methyl radicals at 2 mm. pressure with the other conditions approximately the same as here. The additional width required in our work may perhaps be attributed to the poor condition of a repeatedly used quartz surface, which seems to decrease the sensitivity of lead but not of antimony mirrors.

Table I that these may be 4–10% of the total number of active particles. The corresponding widths of the guard mirrors, w , are included for reference.

In view of the fact that it has already been shown that propionaldehyde seems to desensitize lead mirrors, it is probable that guard mirrors can never be completely effective in stopping alkyl radicals in propionaldehyde vapor, and that the slow removal of guarded antimony mirrors is caused by alkyl radicals. Corresponding experiments with acetone show that guarded antimony mirrors are also removed, but at a much slower rate than experienced with propionaldehyde and only after serious inroads have been made on the lead guard mirror.

TABLE I
CALCULATION OF MAXIMUM FREE HYDROGEN ATOM PRODUCTION FROM DATA ON RATE OF REMOVAL OF GUARDED ANTIMONY MIRRORS

Expt.	144	312	313	314	322
f^a	1.0	0.5	1.0	0.5	0.3
t_{obs} (sec. $\times 10^{-3}$)	5.19	1.62	2.58	2.88	2.70
f_H	.012	.019	.024	.011	.007
d (cm.)	30	24	25.2	33	30
t_{sb} (sec.)	333	262	277	370	333
f_{alk}	.064	.081	.108	.064	.037
w (mm.)	45	50	35	45	65

^a See Part II for key to symbols used.

Part III. Determination of Half-Lives of Free Radicals.—It was found that antimony mirrors could be removed by either propionaldehyde or acetone undergoing pyrolysis or photolysis without the use of a steam jacket. Since consistent times of removal never were obtained with lead mirrors, using propionaldehyde, and only few of the experimental difficulties were encountered with antimony mirrors, only unguarded antimony mirrors were used in half-life studies. It may be shown that the highest possible concentration of free H atoms (see Table I) can have only a small quantitative effect in the determination of the half-life, and does not interfere with identification of the free radicals by this method.

Standard antimony mirrors were deposited in a clean quartz tube at random locations from 4 to 37 cm. away from the light source in all experiments. The 91 quantitative experiments on propionaldehyde summarized in Fig. 2 were conducted at a pressure of 2.54 ± 0.05 mm. at the entrance to the reaction tube and at a temperature of $23 \pm 2^\circ$ along the tube and at the mirrors. The times of removal of mirrors in each cm. length were averaged and these averages were used in

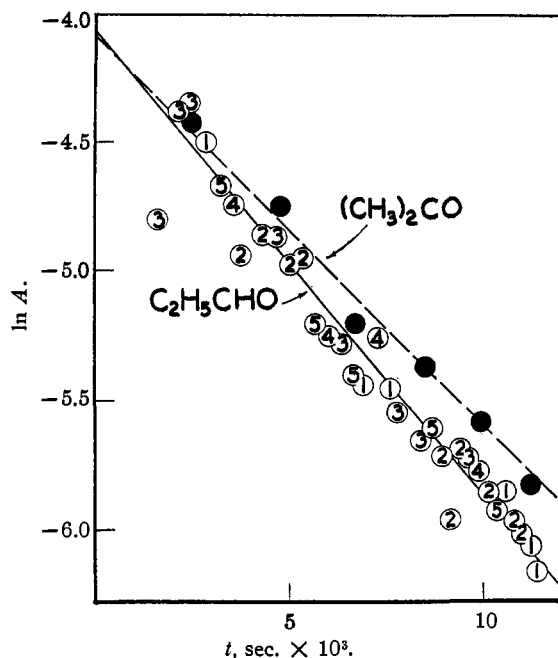


Fig. 2.—The logarithm of mirror "activity" as a function of the time of transport of the radicals in propionaldehyde and acetone. Each point is the average of a number of others. For propionaldehyde the number of values involved in the average is indicated for each point. For acetone the points have approximately equal weights, six or seven values being involved in the average for each.

subsequent plots and calculations. The distance from the light can be translated into time of transport by the use of a formula given by Paneth and Lautsch,¹⁷ where t = time of transport of free

$$t = \frac{X_2 - X_1}{V} - \frac{a}{2VP} (X_2^2 - X_1^2)$$

radicals. In our apparatus, X_1 , the distance from the beginning of the constricted region to the far edge of the irradiated zone, was 20 cm. V , the streaming velocity, was 1790 cm./sec. for both acetone and propionaldehyde at $P = 2.54$ mm. pressure. The pressure gradient, a , along the tube was 0.03 mm. per cm. $X_2 = 20$ cm. plus the distance of the mirror from the lamp. The terminal pressure was taken as 0.1 mm.

Paneth and Lautsch showed that, if A is activity of mirror = reciprocal of time of mirror disappearance, then $\ln A$ plotted against t , the time of transport, will produce an approximately straight line. The half-life is calculated from the slope, k , by means of the relationship

$$t_{1/2} = \ln 2/k$$

The slope of the straight line for propionaldehyde in Fig. 2 is 180, indicating a half-life of 3.8

(17) F. Paneth and W. Lautsch, *Ber.*, **64**, 2708 (1931).

$\times 10^{-3}$ sec. for the free radicals from the photolysis of that compound, in agreement with the value of 3.9×10^{-3} sec. for ethyl radicals given by Paneth and Lautsch.⁷

For purposes of comparison, a series of standard mirror experiments with acetone was conducted at each 6 cm. interval of the tube from the lamp. The results are also plotted in Fig. 2. Since k for this line is 150, the observed half-life of these radicals is 4.6×10^{-3} sec.¹⁸ In view of the fact that this value is based upon data for 38 experiments, the agreement with Paneth's value of 5.8×10^{-3} sec.¹⁹ and Pearson's value of 5.3×10^{-3} sec.⁵ for methyl radicals is not particularly good. A point of immediate interest, however, is that the half-lives of the particles obtained from propionaldehyde and from acetone are significantly different from each other, and the difference is in the direction which corresponds to the difference in the product radicals which may be expected in the two cases.

The question arose, during this investigation, whether or not mirror-active particles were produced by photosensitization; *i. e.*, through action of traces of excited mercury vapor rather than a true photolysis, because the radiation from a lamp of the type used is known to be rich in the 2537 Å. resonance line. To avoid such photosensitization, mercury vapor had been deliberately excluded from the reaction tube J by the liquid nitrogen trap at E and silver turnings at G. For more complete confirmation, a hot wide-tube mercury arc, the Hanovia Sun-Lamp, was used to produce free radicals in propionaldehyde vapor. Three standard antimony mirror experiments were performed, all resulting in mirror removal in approximately nine minutes each. The first experiment was conducted with air cooling. In the second, also with air cooling, the light was filtered through mercury vapor over a pool of the metal immediately beneath the quartz tube. In the third, also with mercury vapor filter, the cooling was omitted.²⁰ The similarity of the results under the three different sets of conditions seems to eliminate the possibility that photosensitization was involved.

Discussion

The fact that the experiments on acetone and on propionaldehyde were conducted under similar

(18) Incidentally, it may be mentioned that when t is plotted against $X_2 - X_1$, the direction of curvature is as reported by Pearson; *cf.* Burton, *ref.* 9a.

(19) F. Paneth and W. Hofeditz, *Ber.*, **62**, 1335 (1929).

(20) *Cf.* T. G. Pearson and R. H. Purcell, *J. Chem. Soc.*, 253 (1936); *Nature*, **136**, 221 (1935).

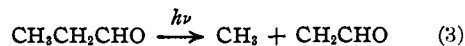
conditions (same velocity, temperature, pressure, and light source) enables a direct comparison to be made between the two compounds. Figure 2 shows that the activity of the free radicals at the lamp exit is the same for the two, within experimental error. Since acetone and propionaldehyde are homologous isomers, free radicals of the same kind should disappear by collision and by wall reaction at the same rate in streams of the two provided that they are not involved in chain reactions. The low quantum yields reported for work at room temperature^{21,2} indicate that there are probably no chains under the conditions of these experiments. Thus, the fact that the rates of disappearance of the free radicals were different is an indication that the radicals were also, to some extent, different.

It already has been shown in Part II above that the guard mirror experiments with propionaldehyde demonstrate that free H atoms comprise less than 2% of the total number of active particles produced and are most probably entirely absent. This result is in agreement with previous work on the photolysis of acetaldehyde,^{9a} which indicates that free H atoms are not produced and that the HCO radical is stable up to 100°.

If we return now to the matter of the 4.6×10^{-3} sec. half-life of the particles resulting from the photolysis of acetone, we see that the agreement with the value of Pearson (5.3×10^{-3} sec.) is not particularly good. Since both our work and that of Pearson are founded on approximately the same number of data, and were performed with presumably the same care, it is possible that the difference in half-lives results from a difference in the conditions of the experiments and of the geometry of the apparatus. If such is the case, the conclusion follows that half-lives determined by us would tend to be low.

This last conclusion suggests that the agreement between our value of 3.8×10^{-3} sec. for the half-life of the products of the photolysis of propionaldehyde and the 3.9×10^{-3} sec. value of Paneth and Lautsch for ethyl radicals (which, incidentally, is for wholly different conditions) is entirely fortuitous and that, for our conditions, the 3.8×10^{-3} sec. value is much higher than would correspond exclusively to ethyl radicals. The obvious explanation is that particles of longer half-life are also present in the photolysis of pro-

pionaldehyde. The maximum concentration of free H atoms which might possibly be present (*i. e.*, 2%) would be inadequate to account for an effect of this magnitude. A more probable cause could be the presence of free methyl radicals formed in the possible reaction



The evidence we have presented is insufficient to resolve the question. However, the problem presents an interesting point for speculation for it clearly involves the mechanism of energy transfer in a photoactivated molecule. In a following investigation it is hoped to establish the nature of the products in a direct manner.

With the exception of formaldehyde, all the aldehydes and ketones have remarkably similar absorption spectra.²² It is therefore to be expected that if free radicals are found in the products of photolysis of one of the lower aldehydes or ketones, they might be found also in the other cases. This expectation has been borne out in the present case. It is interesting that Fig. 2 shows that when acetone and propionaldehyde are similarly illuminated (*i. e.*, with an arc rich in the line $\lambda = 2537 \text{ \AA.}$) approximately equal concentrations of free radicals are produced in the irradiated zone. Herr and Noyes²¹ have recently presented evidence which suggests that the photolysis of acetone under conditions similar to ours is exclusively *via* a free radical mechanism. If we assume approximately the same light absorption by acetone and propionaldehyde in the wave length range used, and if we note, further, that the concentrations of acetone and of propionaldehyde are approximately the same in the irradiated zone in the different experiments, it would follow that the photolysis of propionaldehyde proceeds exclusively by a free radical mechanism.

Summary

1. Free alkyl radicals have been found in the photolysis of propionaldehyde by the Paneth mirror method. The half-life of the particles is 3.8×10^{-3} sec., in good agreement with the value of 3.9×10^{-3} sec. given by Paneth and Lautsch for free ethyl radicals.

2. Similar experiments with acetone produced free radicals having a half-life of 4.6×10^{-3} sec. Acetone is known to produce methyl radicals, the half-life of which has been reported by Pearson as

(21) D. S. Herr and W. A. Noyes, Jr., *THIS JOURNAL*, **62**, 2052 (1940).

(22) P. A. Leighton and F. E. Blacet, *Chem. Rev.*, **17**, 353 (1935.)

5.3×10^{-3} sec. under slightly different conditions.

3. The use of the lead guard-mirror technique has established that free hydrogen atoms certainly comprise less than 2% of the total number of mirror-active particles produced in the photolysis of propionaldehyde and are probably completely absent. The result supports the view that the free formyl radical is stable up to temperatures of 100°.

4. Propionaldehyde and acetone vapors have

the same viscosity under the conditions of temperature and pressure used, and under similar conditions of illumination appear to produce approximately equal concentrations of alkyl radicals. The significance of this result in reference to the mechanism of the photolysis is discussed.

5. The possibility is also discussed that there may be competing free radical decompositions in the photolysis of propionaldehyde.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS AND THE WILLIAMS OIL-O-MATIC HEATING CORPORATION]

Hydrogen Bonding and the Solubility of Alcohols and Amines in Organic Solvents. XIII

BY M. J. COPLEY,¹ E. GINSBERG, G. F. ZELHOFER AND C. S. MARVEL

A study² of the solubilities of the volatile haloforms in donor solvents, free from hydroxyl or amide hydrogens, has shown that large negative deviations from Raoult's law are consistently observed. This behavior has been explained by the assumption that on mixing, intermolecular association of unlike molecules occurs through the mechanism of C—H←N or O bonds. Recent infrared absorption studies by Buswell, Roy, and Rodebush³ and by Gordy⁴ have confirmed this picture.

It is also desirable to make studies of the solubilities of volatile alcohols and amines in a variety of types of organic liquids containing donor atoms. Such studies would furnish further information on the influence of solute and solvent association on solubility. A comparison of the solubilities of an alcohol in a series of solvents containing different functional groups should give the relative strengths of the donor atoms. It is of interest to determine whether this relative order is the same as was observed for the haloforms in the same type of solvents. Gordy⁵ has determined the shift of the OD fundamental frequency when CH₃OD is mixed with a series of

different donor solvents. A relation should exist between his data and the relative solubilities of alcohols in similar solvents.

Experimental

The method used in making the solubility measurements is the same as that described in a previous paper⁶ except that the lower vapor pressures involved made it advisable to substitute an oil or mercury manometer for the pressure gage. The materials used were all purified carefully by chemical means and fractional distillation where feasible. Solubility measurements were made over a range of pressures at a temperature of 32.2°. For comparative purposes, the solubilities at a partial pressure corresponding to the vapor pressure of the solute at 4.5° are used in Tables II and III and in the discussion. The vapor pressures of a number of the solutes at temperatures other than their boiling points which had not been previously reported in the literature were measured experimentally. Vapor pressures were determined at a number of different temperatures and a plot of logarithm of the pressure against 1/T°K. was made. The vapor pressures tabulated in Table I were calculated from these plots.

TABLE I
VAPOR PRESSURES OF SOLUTES

	V. p. at 4.5°, mm.	V. p. at 32.2°, mm.
<i>s</i> -Butyl alcohol	5.5	31
<i>i</i> -Propylamine	223	743
<i>n</i> -Propylamine	106	397
Diethylamine	88	316
<i>s</i> -Butylamine	56.5	287.5
<i>i</i> -Butylamine	45.4	199
<i>n</i> -Butylamine	24	105

In Tables II and III the "ideal" or theoretical mole fraction solubility was calculated using Raoult's law, and is the ratio of the vapor pressure of the solute at 4.5° to its

(1) Present address, Eastern Regional Research Laboratory, U. S. Department of Agriculture, Chestnut Hill Station, Philadelphia, Pennsylvania.

(2) (a) Zellhoefer, Copley, and Marvel, *THIS JOURNAL*, **60**, 1337 (1938); (b) Zellhoefer and Copley, *ibid.*, **60**, 1343 (1938); (c) Copley, Zellhoefer, and Marvel, *ibid.*, **60**, 2666 (1938); (d) Copley, Zellhoefer, and Marvel, *ibid.*, **61**, 3550 (1939).

(3) Buswell, Roy, and Rodebush, *ibid.*, **60**, 2528 (1938).

(4) (a) Gordy, *ibid.*, **60**, 605 (1938); (b) *J. Chem. Phys.*, **7**, 163 (1939).

(5) (a) Gordy, *ibid.*, **7**, 93 (1939); (b) Gordy and Stanford, *ibid.*, **8**, 170 (1940).

(6) G. F. Zellhoefer, *Ind. Eng. Chem.*, **29**, 584 (1937).