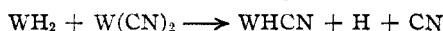


meters and minutes appearing in column 7 of Table II-C. The low value for the one run with a 3-1 initial ratio of hydrogen to cyanogen is understandable since by the end of the run practically all the cyanogen has reacted. Bodenstein-Lind constants, however, fit the variation with respect to total pressure at 675°, and the fit would be better if a lower value of *m* were taken for this temperature; but they are totally unsatisfactory at 625°.

Since there is no reason to suppose that the steps in chain propagation are any different in the clean bulb, the increased rate at low temperatures along with the lower temperature coefficient argues for a different method of chain starting on the surface. The possibility



which results in the foregoing kinetic expression suggests itself since Hadow and Hinshelwood¹¹ obtained evidence of strong adsorption of cyanogen on clean silica in their oxidation studies.

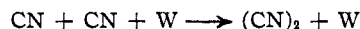
Hogness and T'sai¹⁰ found that CN radicals disappear at room temperature by addition to cyanogen molecules to form a postulated (CN)₃ which acts as a nucleus for further polymerization with the ultimate formation of paracyanogen. White⁹ concluded that the radicals formed during an electric discharge combine with complex ions simultaneously produced in the discharge as a first step in polymerization. In the present investigation at temperatures of 625° or higher such an addition reaction was not indicated by kinetic analysis of the results in the aged bulb,

(11) H. J. Hadow and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A132**, 375 (1931).

nor was any extensive polymerization observed. This must mean that the reactions



and



are much faster than the addition of radical to molecule. It may well be that the (CN)₃ complex is unstable at these temperatures since it is known that cyanogen does not polymerize at elevated temperatures and that paracyanogen begins to regenerate cyanogen in the region 700-800°.

Summary

The thermal reaction of hydrogen and cyanogen to yield hydrogen cyanide has been studied in a silica vessel over the temperature range 550-675°. The reaction proceeds without undue complications, but the nature of the surface of the reaction bulb has some influence on the rate. The product, hydrogen cyanide, inhibits the reaction. Packing increases the rate at low temperatures but has little effect above 625°.

The simplest expression which fits the kinetics at 625° reasonably well is that developed by Bodenstein and Lind for the combination of hydrogen and bromine. Evidence is presented which favors a radical chain mechanism involving gas phase propagation by hydrogen atoms and cyanide radicals with chains starting and breaking on the walls. The steps in this process would be analogous to those in the hydrogen-bromine reaction with the cyanogen assuming the role of bromine.

PRINCETON, NEW JERSEY

RECEIVED MAY 6, 1942

[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

The Ternary Systems Involving Cyclohexane, Water, and Isopropyl and Normal Propyl Alcohols

BY E. ROGER WASHBURN, CHARLES E. BROCKWAY, C. LOREN GRAHAM AND PHILIP DEMING

The ternary systems¹ made up of cyclohexane, water, and^{1a} methyl and^{1b} ethyl alcohols have been described previously.

The systems² involving water, isopropyl alcohol and^{2a} benzene,^{2b} toluene and^{2c} cyclohexene have been described.

(1) E. R. Washburn, *et al.*, *THIS JOURNAL*, (a) **56**, 361 (1934); (b) **54**, 4217 (1932).

(2) E. R. Washburn, *et al.*, *ibid.*, (a) **57**, 303 (1935); (b) **62**, 579 (1940); (c) **62**, 1454 (1940).

This report adds normal propyl and isopropyl alcohols to the first group and cyclohexane to the second group.

Materials.—Cyclohexane from Eastman Kodak Company was carefully fractionated, dried with sodium and recrystallized several times. The alcohols were the best grades obtainable from the same company. They were dried with active lime and carefully fractionated. Some physical

constants for the materials used in this investigation are recorded in Table I.

TABLE I

Material	Specific gravity, d_{25}^{25}	Refractive index, n_{25}^{25}	Freezing point, °C.
Cyclohexane	0.7746	1.4232	6.1°
<i>n</i> -Propyl alcohol	.8000	1.3838	..
Isopropyl alcohol	.7808	1.3749	..

^a A small amount of cyclohexane resulting from many recrystallizations had a freezing point of 6.33° and a specific gravity, d_{25}^{25} , of 0.7744, and a refractive index not measurably different from that recorded above. This more highly purified material was employed in four solubility measurements with *n*-propyl alcohol and water at 35°. The differences in the results obtained with the 6.1° and the 6.33° cyclohexane, both for the solubility determinations and the refractive index-composition relationships, were well within the experimental errors.

Procedure and Results.—The experimental procedures were essentially the same as those which have been described.^{1,2} The results are presented in the following tables and graphs. Since the concentrations are presented in weight per cent., it will be enlightening to state that in each solubility determination and in each dis-

TABLE II

n-PROPYL ALCOHOL, CYCLOHEXANE AND WATER AT 25.0°

Cyclohexane, wt. %	<i>n</i> -Propyl alcohol, wt. %	Refractive index	Cyclohexane, wt. %	<i>n</i> -Propyl alcohol, wt. %	Refractive index
92.41	7.30	1.4192	17.77	58.73	1.3825
84.09	14.98	1.4152	12.91	57.60	1.3788
75.60	22.55	1.4114	6.56	49.52	1.3708
66.73	29.87	1.4071	4.29 ^a	43.01	1.3660
56.64	37.94	1.4027	2.16 ^a	35.63	1.3608
46.57	45.22	1.3974	0.72 ^a	27.42	1.3550
36.81	51.50	1.3930	0.08 ^a	18.49	1.3488
26.95	56.68	1.3880	0.06 ^a	9.40	1.3408
Water saturated with cyclohexane			1.3322		
Cyclohexane saturated with water			1.4233		

^a Mixtures of *n*-propyl alcohol and water were titrated with cyclohexane.

TABLE III

n-PROPYL ALCOHOL, CYCLOHEXANE AND WATER AT 35.0°

Cyclohexane, wt. %	<i>n</i> -Propyl alcohol, wt. %	Refractive index	Cyclohexane, wt. %	<i>n</i> -Propyl alcohol, wt. %	Refractive index
92.06	7.62	1.4137	18.05	58.91	1.3792
84.21	14.86	1.4101	13.14	57.99	1.3758
75.60	22.54	1.4062	7.42 ^a	51.60	1.3692
67.04	29.81	1.4026	4.19 ^a	42.96	1.3692
57.29	37.48	1.3982	2.21 ^a	34.87	1.3579
46.54	45.27	1.3937	0.85 ^a	27.46	1.3528
37.31	51.40	1.3893	0.11 ^a	18.40	1.3467
26.96	56.68	1.3844	0.07 ^a	9.21	1.3392
Water saturated with cyclohexane			1.3311		
Cyclohexane saturated with water			1.4177		

^a Mixtures of *n*-propyl alcohol and water were titrated with cyclohexane.

TABLE IV

ISOPROPYL ALCOHOL, CYCLOHEXANE AND WATER AT 25.0°

Cyclohexane, wt. %	Iso-propyl alcohol, wt. %	Refractive index	Cyclohexane, wt. %	Iso-propyl alcohol, wt. %	Refractive index
0.14	8.80	1.3400	18.97	55.74	1.3778
0.32	23.88	1.3531	26.85	53.53	1.3848
1.08	36.80	1.3616	35.97	49.29	1.3897
4.81	48.29	1.3687	43.56	45.08	1.3936
10.46	53.88	1.3739	55.02	37.86	1.3995
16.27	55.57	1.3777	71.40	25.78	1.4066
			86.98	12.82	1.4144

TABLE V

CONJUGATE SOLUTIONS CONTAINING *n*-PROPYL ALCOHOL AT 25.0°

Water layer			Cyclohexane layer		
Refractive index	Alcohol, wt. %	Water, wt. %	Refractive index	Alcohol, wt. %	Water, wt. %
1.3377	5.8	94.1	1.4228	0.9	0.0
1.3403	8.6	91.1	1.4225	1.4	0.0
1.3450	13.9	85.6	1.4208	4.4	0.0
1.3480	17.5	81.9	1.4167	12.1	0.7
1.3494	19.3	79.9	1.4120	21.3	1.7
1.3505	20.8	78.5	1.4002	41.6	6.7
1.3513	21.9	77.3	1.3922	52.6	12.4
1.3521	23.0	75.9	1.3862	57.8	18.5
1.3636	39.6	57.2	1.3680	45.7	49.2

TABLE VI

CONJUGATE SOLUTIONS CONTAINING *n*-PROPYL ALCOHOL AT 35.0°

Water layer			Cyclohexane layer		
Refractive index	Alcohol, wt. %	Water, wt. %	Refractive index	Alcohol, wt. %	Water, wt. %
1.3365	6.2	93.7	1.4172	1.1	0.0
1.3384	8.3	91.6	1.4168	1.8	0.1
1.3426	13.3	86.7	1.4142	6.7	0.2
1.3448	16.1	84.0	1.4105	14.1	0.8
1.3460	17.7	82.4	1.4050	25.0	2.3
1.3470	19.0	81.0	1.3954	42.6	6.8
1.3480	20.3	79.6	1.3875	53.6	13.0
1.3494	22.3	77.4	1.3812	58.6	20.3
1.3588	36.4	61.2	1.3664	48.0	46.5

TABLE VII

CONJUGATE SOLUTIONS CONTAINING *i*-PROPYL ALCOHOL AT 25.0°

Water layer			Cyclohexane layer		
Refractive index	Alcohol, wt. %	Water, wt. %	Refractive index	Alcohol, wt. %	Water, wt. %
1.3356	4.4	95.4	1.4233	0.0	0.0
1.3383	7.1	92.8	1.4231	0.2	0.0
1.3465	15.4	84.1	1.4223	1.3	0.1
1.3545	25.9	73.9	1.4190	5.9	0.2
1.3590	32.6	66.5	1.4154	11.2	0.3
1.3647	41.6	55.7	1.4117	17.2	1.0
1.3718	52.1	39.9	1.4066	25.8	2.8
1.3789	55.5	26.7	1.4021	33.5	5.4

tribution study the total weight of liquids employed was of the order of 13 to 15 g.

The earlier investigations² of ternary systems containing isopropyl alcohol, water and the hydrocarbons benzene, toluene and cyclohexane showed

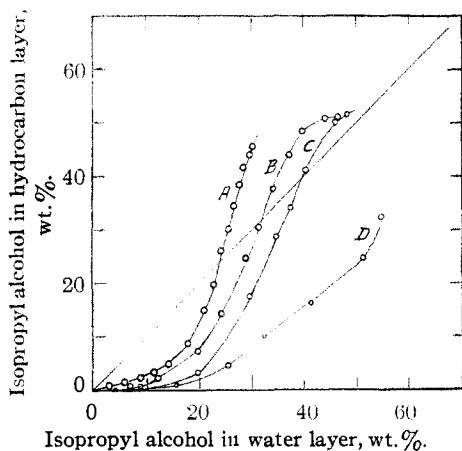


Fig. 1.—A, Benzene; B, toluene; C, cyclohexene; D, cyclohexane.

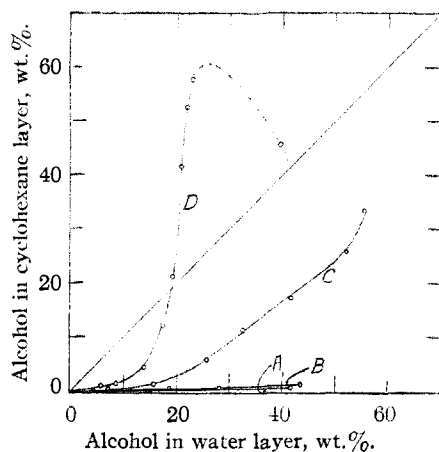


Fig. 2.—A, Methyl alcohol; B, ethyl alcohol; C, isopropyl alcohol; D, *n*-propyl alcohol.

that the greatly increasing proportions in which the alcohol entered the hydrocarbon layer as the total amount of alcohol in the system was increased caused a change in the direction of slope of the tie lines. It will be noted in the present study that, while the proportion of alcohol in the cyclohexane layer increases as the total amount of alcohol increases, it does not ever become equal to the proportion of alcohol in the conjugate layer which is rich in water. The tie lines never become horizontal and the plait point is some distance down on the cyclohexane branch of the binodal solubility curve. Experimental difficulties prevented a very close approach to the plait point and a study of the conjugation curves⁸ did not greatly improve the situation. It is probably not far from 48% alcohol on the cyclohexane arm of the curve.

It should be mentioned that extensions of the tie lines for this system do not converge at a single

point. Attention has been called to the fact that in several ternary systems such convergence is to be observed.⁴ The system methyl alcohol-cyclohexane and water when studied at 25.0°^{1a} not only shows such convergence but the point at which the tie lines converge is practically the cyclohexane vertex of the ternary diagram. The solubility of methyl alcohol in cyclohexane is not only limited but very small. As would be expected, ethyl alcohol^{1b} is between methyl alcohol and the propyl alcohols in its distribution. It is not much different from methyl alcohol.

The systems in which the tie lines change direction of slope represent extreme cases of non-convergence. In one of the earlier studies the distribution of isopropyl alcohol between water and cyclohexene^{2c} was investigated at three different temperatures, 15, 25 and 35°. The slopes of the tie lines and the positions of the plait points changed to a marked extent with the change in temperature. Larger proportions of the alcohol entered the hydrocarbon layer at the higher temperatures. If the present system behaves in a similar manner it might be expected that a change in direction of slope of the tie lines would be observed at a temperature somewhat higher than 25°.

The other system, described in this report, involving *n*-propyl alcohol shows such a change in the direction of slope of the tie lines at 25 and 35°. The change causes the plait point to appear on the opposite branch of the binodal curve from that which would be predicted by the tie lines obtained with the smaller total proportions of the alcohol. It was possible to determine the plait point quite accurately with this system; it appeared at about 42% alcohol on the water branch at 25°. The change of temperature to 35° did not cause as large a change in plait point as was observed in the former system.

The proportions in which these alcohols are distributed between the water and the hydrocarbon layers for these and related systems are clearly shown in Figs. 1 and 2.

Summary

The solubility relationships for the ternary system containing water, cyclohexane and isopropyl alcohol have been determined at 25°. The system containing water, cyclohexane and *n*-propyl alcohol has been studied at 25 and 35°.

LINCOLN, NEBRASKA

RECEIVED JUNE 3, 1942

(4) A. V. Braucker, T. G. Hunter and A. W. Nash, *Ind. Eng. Chem., Anal. Ed.*, **12**, 35 (1940).

(3) "International Critical Tables," Vol. III, p. 398.