Intermediates.—The compounds 2-acetylthiophene, 2-propionylthiophene, 2-butyrylthiophene, 2-butyrylfuran and 2-acetylfuran were prepared according to Heid and Levine[7] by interaction of thiophene (or furan) with the appropriate acid anhydride in the presence of boron trifluoride. Application of this method was extended to prepare 2,5-dimethyl-3-acetylthiophene,[8] 2,5-dimethyl-3-acetylfuran[9] and 2-butyrylpyrrole[10] in yields of 50, 70 and 16.5%, respectively. The physical constants of these compounds were found to be in agreement with those reported in the literature. Treatment of 2,5-dimethyl-2-acetylfuran with excess aqueous ammonia in a sealed tube at 145° for four hours gave the corresponding pyrrole.[9] Decarboxylation of the appropriate keto acids according to the procedure of Burrus and Powell[11] gave 2-acetylpyridine, 4-acetylpyridine, 3-acetylpyridine and 3-propionylpyridine. Application of this method was extended without modification to prepare 3-butyrylpyridine[12] in approximately 15% yields. Interaction of nicotinoyl chloride and benzene in the presence of aluminum chloride gave good yields of 3-benzoylpyridine.[13] Pyridine-3-carboxaldehyde was prepared by the procedure of Panizzon.[14] Thiophene-2-carboxaldehyde was purchased from the Arapahoe Chemical Co., Boulder, Colorado.

Acknowledgment.—We are indebted to David Regenbogen and Sydney Gister for the preparation of intermediates and to Ruth Becker for microanalytical data.

---

[7] J. V. Heid and R. Levine, *J. Org. Chem.*, **13**, 409 (1948).

[8] H. Ruffi, *Ber.*, **20**, 1750 (1887); W. Steinkopf and I. Schubart, *Ann.*, **424**, 1 (1921).

[9] G. Magnanini and T. Bentivoglio, *Gazz. chim. ital.*, **24**, 435 (1894).

[10] B. Oddo, *Ber.*, **43**, 1012 (1910).

[11] H. O. Burrus and G. Powell, THIS JOURNAL, **67**, 1468 (1945).

[12] C. Engler, *Ber.*, **24**, 2541 (1891).

[13] R. Wolffenstein and F. Hartwich, *ibid.*, **48**, 2043 (1915).

[14] L. Panizzon, *Helv. Chim. Acta*, **24**, 24E (1941).

THE RESEARCH LABORATORIES OF THE
NEPERA CHEMICAL CO., INC.
NEPERA PARK, YONKERS, N. Y.

RECEIVED APRIL 25, 1951

Molar Refractions in the Binary System Acetone–Carbon Tetrachloride

BY KENNETH C. BACHMAN[1] AND EDWARD L. SIMONS[2]

In connection with vapor–liquid equilibrium studies of the binary system acetone–carbon tetrachloride, both densities and refractive indices of known solutions covering the entire composition range were made at 25°.[3] In Table I are shown the molar refractions obtained from these data along with those calculated assuming a linear variation with composition.

In spite of the large positive deviations from ideal behavior indicated by the vapor–liquid equilibrium data, the deviations from additivity of the molar refractions, though varying with composition, never exceed 0.045 cc. This observation is in agreement with the more limited data (0–40 mole per cent. acetone) of Smyth, Engel and Wilson[4] and with the unpublished results of Koenig-Gressman.[5]

TABLE I

MOLAR REFRACTIONS IN THE SYSTEM ACETONE–CARBON TETRACHLORIDE

$$[\mathrm{R}]_{\mathrm{D}},\ \text{obsd.} = \left(\frac{n^2 - 1}{n^2 + 2}\right) \times \left(\frac{x_1M_1 + x_2M_2}{d}\right);\ [R]_{\mathrm{D}},\ \text{calcd.} = 16.167 + 10.280x_2.$$

Mole fraction CCl_4, x_2	Molar refraction $[R]_D$ obsd.	Molar refraction $[R]_D$ calcd.	ΔR
1.000	26.447	(26.447)	
0.8978	24.426	25.396	0.030
.8027	24.461	24.419	.042
.6990	23.394	23.353	.041
.5993	22.371	22.328	.043
.4996	21.345	21.303	.042
.4005	20.309	20.284	.025
.3010	19.292	19.261	.031
.2004	18.250	18.227	.023
.1003	17.212	17.198	.014
.0000	16.167	(16.167)	

---

[1] M. W. Kellogg Co., Jersey City, N. J.

[2] General Electric Research Laboratory, Schenectady, N. Y.

[3] K. C. Bachman and E. L. Simons, *Ind. Eng. Chem.*, Jan. (1952).

[4] C. P. Smyth, E. W. Engel and E. B. Wilson, Jr., THIS JOURNAL, **51**, 1736 (1929).

[5] M. L. Koenig-Gressman, Thesis, University of Munich, 1938. Data obtained through courtesy of Prof. K. Fajans.

SCHOOL OF CHEMISTRY
RUTGERS UNIVERSITY
NEW BRUNSWICK, N. J.

RECEIVED APRIL 13, 1951

The Failure of Crystalline Vitamin B_{12} to Exchange with Co^{60} in Acidic and Neutral Aqueous Solutions

BY R. R. BALDWIN, J. R. LOWRY AND R. V. HARRINGTON

Because of the recent availability and interest in the growth-promoting characteristics and metabolism of vitamin B_{12}, it was decided to determine whether a radioactive form of the vitamin could be prepared for study by simple exchange with Co^{60}, over a period of several weeks. Fantes, Page, Parker and Smith[1] have shown that this exchange does not occur over a period of two hours at room temperature in 0.1 *N* acid or alkali, or by boiling for one hour at *p*H 7. However, the possibility of exchange on prolonged contact has not been examined.

The possibility of such an exchange was indicated by application of paper chromatography. $Co^{60}SO_4$ in solution with B_{12} was observed to migrate with B_{12}, while a control spot of $Co^{60}SO_4$ did not migrate. To determine whether this is an actual exchange or simply a weak complexing or surface action, the following experiment was performed.

The approximate analysis of the cobalt content of B_{12} is 4%.[2] An aqueous solution was prepared containing 0.1 mg./ml. crystalline Merck vitamin B_{12}. Approximately ten times the amount of cobalt present in the B_{12} was added in the form of $Co^{60}SO_4$. The mixture was allowed to stand at room temperature for five weeks at a *p*H of about 2. This B_{12} cobalt mixture exhibited growth stimulation on *Lactobacillus leichmannii* (ATC 4797). Model experiments had indicated that B_{12} could be salted out of water and into *n*-butanol by the addition of solid ammonium sulfate. Cobalt under these conditions remained in the aqueous phase. Repeated application of the salting-out procedure to the radioactive mixture resulted in a final butanol phase, strongly colored by the vitamin but exhibiting no radioactivity. This procedure was repeated with a neutral solution of B_{12} and $Co^{60}SO_4$ with the same negative results.

The experimental results are recorded in Table I.

A thin-window counting tube was employed in the measurements. Accordingly, under the above conditions, vitamin B_{12} does not exchange with radioactive cobalt, and the conclusions of Fantes, *et al.*, concerning the strong coördinate

---

[1] K. H. Fantes, J. E. Page, L. F. J. Parker and E. L. Smith *Proc. Roy. Soc. (London)*, [B]**136**, 592 (1949).

[2] E. L. Rickes, N. G. Brink, F. R. Koniuszy, T. R. Wood and K. Folkers, *Science*, **108**, 134 (1948).