Experimental

Absorption Spectra.—These were measured by Earl Gregg and John Efroymson with a Beckman quartz spectrophotometer, Model DU.

4-Methyl-3,4,5,6-tetrahydrophthalic Acid.—Compound I was prepared in nearly theoretical crude yield according to Wicks, Daly and Lack from a sample of the adduct (m. p. 178–182°). After extraction with an equal volume of boiling water it froze at about −40° and melted at about −10°. It was sharply dibasic. When the titration solution was concentrated and acidified with excess concentrated hydrochloric acid in the presence of benzene, crystals of the acid corresponding to I formed readily. They were washed with benzene and a small amount of water. They melted at 125–126° with decomposition when heated rapidly.

Anal. Calcd. for $C_9H_{12}O_4$: C, 58.66; H, 6.57; neut. equiv., 92.0. Found: C, 58.74; H, 6.75; neut. equiv., 92.5.

The melting point of I when prepared by distilling this acid was found to be −5°. Crude and pure I had the same refractive index, n^{20}_D 1.5002.

Anal. Calcd. for $C_9H_{10}O_3$: C, 65.02; H, 6.08. Found: C, 65.03; H, 5.98.

When the pure anhydride was reconverted to the acid the yield amounted to 80% and when the crude anhydride was used to only 55–72%. These low yields are believed due in part to the instability of the acid.

4-Methylphthalic Anhydride.—An authentic specimen was prepared from the isoprene–maleic anhydride adduct by the sulfur dehydrogenation method which Newman[6] used for preparing 3-methylphthalic anhydride from the piperylene adduct. The yield of 4-methyl derivative amounted to 59% of a product which melted at 91–92°. Mayer and Gunther[7] reported 92°. The bromine dehydrogenation of 5.0 g. of crude I according to Newman and McCleary[2] resulted in a yield of 0.8 g. (16%) of crystals, m. p. 91–92° alone or mixed with the authentic specimen. Efforts to isolate 3-methylphthalic anhydride from the mother liquors were not successful.

Dehydrogenation of crude I with sulfur (2 moles per mole of I) during thirty minutes at 240–260° supplied a 7% yield of 4-methylphthalic acid melting at 150–151°. This acid was isolated by acidifying the alkaline extract of the reaction product. No evidence could be found for the presence of 3-methylphthalic acid or of 3-methylphthalic anhydride.

The Hydrogenation of I.—Sixteen and six-tenths grams (0.1 mole) of crude I, 100 ml. of ethyl acetate and 20 g. of Raney nickel were shaken at three atmospheres pressure of hydrogen and at 25° for seventy-two hours. During this time 0.09 mole of hydrogen was absorbed. The Raney nickel which had been stored under water was washed with alcohol and then with ethyl acetate just prior to use. The catalyst was filtered off and most of the solvent distilled away. The crystals which formed in the remaining filtrate when it was cooled were filtered off and washed with ethyl acetate. They melted at 170–175° and, including a small amount recovered from the hydrolysis of the anhydride in the filtrate, weighed 7.6 g. (41%). Recrystallization from dilute alcohol raised the m. p. to 177–179° and this was not depressed by admixture with authentic *trans*-4-methylhexahydro-*cis,cis*-phthalic acid.[3]

Summary

The main component in the pyrolysis product of the sorbic acid–maleic anhydride adduct has been found to be 4-methyl-3,4,5,6-tetrahydrophthalic anhydride. Saponification yielded the salt of the corresponding acid and hydrogenation accompanied by hydrolysis yielded *trans*-4-methylhexahydro-*cis,cis*-phthalic acid.

BRECKSVILLE, OHIO RECEIVED DECEMBER 19, 1949

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(6) Newman, This Journal, **59**, 1004 (1937).

(7) Mayer and Gunther, *Ber.*, **63**, 1458 (1930).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Frontal Analysis of Ethers and Sulfides

BY CHARLES D. HURD, GEORGE R. THOMAS[1] AND ARTHUR A. FROST

Indifferent compounds such as ethers or sulfides may often be separated from mixtures by distillation, but one can visualize mixtures where this approach is closed, as with ethyl hexyl ether and 1,2-diethoxyethane, both of which boil at 119°. Thermal instability may also invalidate distillation analysis, as in sulfide mixtures containing mustard gas, since the latter, on heating, is reported[2] to change into 1,8-dichloro-3,6-dithiaoctane, $ClCH_2CH_2SCH_2CH_2SCH_2CH_2Cl$, 1,11-dichloro-3,6,9-trithiahendecane, $(ClCH_2CH_2SCH_2CH_2)_2S$, and other products.

Analysis of mustard gas by chemical methods is difficult also. Thus, the method of Rosser, Meade and Glover reported by Fuson[2] was carried out by treating the 2-chloroethyl sulfide with sodium methyl sulfide followed by distillation of the methyl mercapto derivative. According to Meade and Moggridge,[3] however, this reaction gives rise not only to the expected (2-methylmercapto)-ethyl sulfide, $(CH_3SCH_2CH_2)_2S$, but also to about 1% of 2,5,8,11-tetrathiadodecane, $CH_3S{-}(CH_2CH_2S)_3{-}CH_3$, and 0.02% of 2,5,8,11,14-pentathiapentadecane, $CH_3S{-}(CH_2CH_2S)_4{-}CH_3$. These investigators pointed out that analyses of mixtures such as $Cl(CH_2CH_2S)CH_2CH_2Cl$, $Cl(CH_2CH_2S)_2CH_2CH_2Cl$ and $Cl(CH_2CH_2S)_3CH_2CH_2Cl$ by this method "can at best only be regarded as rough approximations."

Adsorption analysis seemed well suited for such mixtures. It was first planned in the present study to analyze mixtures containing mustard gas by chromatographic adsorption after first converting the chloro sulfide into *p*-phenylazophenoxyethyl sulfide, $(PhN{=}N{-}C_6H_4{-}O{-}CH_2CH_2)_2S$, by reaction with the sodium salt of *p*-hydroxyazobenzene. Although it was possible to obtain this orange derivative, m. p. 151°, in good

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[1] Department of Chemistry, Boston University, Boston, Massachusetts.

(2) Fuson, Lipscomb, McKusick and Reed, *J. Org. Chem.*, **11**, 513 (1946).

(3) Meade and Moggridge, *J. Chem. Soc.*, 813 (1946).

yield (refluxing one hour in alcohol solution, then evaporating to dryness, and crystallizing from acetone–water), it was established that appreciable quantities of other products were formed. Thus, 0.37 g. of the crude derivative (uncrystallized) was taken up in chloroform, washed four times with 20% sodium hydroxide solution to remove any unused hydroxyazobenzene, then with dilute sulfuric acid, finally with sodium bicarbonate solution. The chloroform layer was dried (sodium sulfate) and poured into a column of silica gel, prepared as described by Hurd and Zelinski.[4] The adsorbed material was eluted by passing a 1:1 mixture of benzene and ligroin (b. p. 80–100°) through the column. An upper band contained 0.073 g. of yellow solid which melted up to 110°. The contents of a lower yellow band, 0.296 g., melted at 150.0–151.5°. Evidently the interfering side reactions reported by Meade and Moggridge[3] were also operating here.

Frontal analysis was then tried. This method avoided the above-mentioned difficulty of side reactions in the preparation of derivatives, since it analyzed the material as such.

The frontal method has been discussed at length by Claesson.[5] In this method, a solution of the mixture to be analyzed is passed through an adsorption column. The adsorbent in the column becomes saturated with respect to each of the components of the mixture after different volumes of the solution have passed through it. Each time the column becomes saturated with respect to a component, a change in the refractive index of the eluate occurs. The volume of the eluate is plotted automatically against the refractive index. The sharp change in refractive index corresponds to a new component appearing in the eluate. Claesson developed formulas (1) and (2)

$$C_{\mathrm{i.m}} = C_{\mathrm{i.m-1}} - \frac{f_{\mathrm{i}}(C_{\mathrm{i.m-1}}, \cdots) - f_{\mathrm{i}}(C_{\mathrm{i.m}}, \cdots)}{V^0_{\mathrm{m}}} \quad (1)$$

for component *i* at step *m*, with V^0_m representing the retention volume in the column per gram of adsorbent for step *m* at which point the column becomes saturated with respect to this component, and C_i representing concentration of *i* in the front for the step in question.

$$C_{\mathrm{i.m+1}} = C_{\mathrm{i.m}} \left(1 - \frac{k_{\mathrm{i}}}{k_{\mathrm{m}}} \cdot \frac{V^0_{\mathrm{m}}}{V^0_{\mathrm{m+1}}}\right) \Big/ \left(1 - \frac{k_{\mathrm{i}}}{k_{\mathrm{m+1}}}\right) \quad (2)$$

for component *i* at step $m + 1$ where k_i stands for the constant in Langmuir's adsorption isotherm in the form: $f_i = k_iC_i/(1 + l_iC_i)$. Using equation 2 Claesson was able to identify qualitatively and estimate quantitatively the amount of each component in the original solution.

In the present investigation the adsorption of mixtures of ethers and sulfides was studied on silica gel and alumina as adsorbents, these mixtures being selected: butyl ether and 1,2-diethoxyethane; propyl sulfide and 1,2-bisethylmercaptoethane; 2-chloroethyl sulfide and 1,8-dichloro-3,6-dithiaoctane.

Materials.—The silica gel was obtained as "Commercial Grade," 28–200 mesh from the Davison Chemical Company. Alumina was the Alcoa Commercial Grade, 60–100 mesh.

Cyclohexane solvent was purified by taking 1500 ml. of the technical grade (m. p. 2°) and adding 100 ml. of nitrating reagent consisting of 70 ml. concentrated sulfuric acid and 30 ml. concentrated nitric acid. The mixture was placed in an ice-bath and was stirred vigorously for fifteen minutes. The temperature of the reaction mixture was then allowed to rise to 25° during one hour. The cyclohexane was then decanted, washed thrice with 100 ml. of 25% sodium hydroxide, thrice with 100 ml. of water, then was dried over calcium chloride and distilled. This material melted at 5.5°. The process was repeated, giving a product melting at 5.8° (uncor.). The cyclohexane was passed through an 8-cm. bed containing 20 g. of Davison silica gel. The final product melted at 5.8° (uncor.).

The solutes (adsorbates) were purified before use. These constants (b. p. uncor.) were obtained on the purified materials: butyl ether, b. p. 138.5°; 1,2-diethoxyethane, b. p. 118–119°; propyl sulfide, b. p. 141–143°; 1,2-bis-(ethylmercapto)-ethane, $C_2H_5SCH_2CH_2SC_2H_5$, b. p. 120° (40 mm.); 2-chloroethyl sulfide, $(ClCH_2CH_2)_2S$, b. p. 95–97° (8 mm.); 1,8-dichloro-3,6-dithiaoctane,[6] $(ClCH_2CH_2SCH_2—)_2$, m. p. 47–48°.

Apparatus.—A continuously recording flow refractometer described elsewhere[7] was used. The sensitivity was adjusted so that 0.002 unit change in refractive index gave full-scale deflection on the G. E. photoelectric recorder. The column and the method of flow control is schematically represented in Fig. 1. The ground-glass joint fitted into a ground-glass counterpart in the refractometer. The air vent allowed the air from the column to escape before the eluate passed into the refractometer. The column was constricted to hold a small wad of glass wool which supported the column of adsorbent. The column was made of Pyrex tubing, 45 cm. long and 10 mm. outside diameter. Sealed to the top of the column was an Erlenmeyer flask designated as reservoir 2. Above this was reservoir 1 as diagrammed. This arrangement kept a constant flow rate to about 3 parts per 1000, since the liquid level in reservoir 2 was automatically maintained between X and X′, a variation of about 2 mm.

Method.—A piece of glass wool was placed into the constriction. The column was held at an angle of 45° and the adsorbent was placed in reservoir 2 and covered with cyclohexane. The solvent was heated to boiling to expel air occluded in the gel. The column was then turned to the vertical position and swirled so that the gel would settle into the column. The gel settled rapidly to form a bed. The column was then attached to the refractometer, and reservoir 1, filled with 250 ml. of solution to be analyzed, was set in place. As soon as the excess solvent from the packing of the column drained to the top of the column, the solution was admitted from reservoir 1 into 2, at which time the meter chart was started.

Discussion of Results.—Duplicate experiments were performed with two different columns of the same adsorbent. It was established that values of L_1/L_2 were reproducible to ±1.0% with silica as adsorbent and ±1.5% with alumina.

Known mixtures of butyl ether and 1,2-diethoxyethane in cyclohexane were passed through the silica adsorbing column. The results of four such runs are given in Table I. Five to eight grams of silica gel was used in each run. The

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(4) Hurd and Zelinski, THIS JOURNAL, **69**, 243 (1947).

(5) Claesson, *Arkiv. Kemi, Mineral., Geol.*, **23A**, No. 1, 1-133 (1946;) *Annals N. Y. Acad. Sci.*, **49**, 183-208 (1948).

(6) Bennett and Whincop, *J. Chem. Soc.*, **119**, 1860 (1921), list 54°; Price and Roberts, *J. Org. Chem.*, **12**, 265 (1947), report 46-50°.

(7) Thomas, O'Konski and Hurd, *Anal. Chem.*, **22**, in press (1950).

TABLE I

DATA FOR FRONTAL ANALYSIS OF MIXTURES

Mixtures: I, B, Bu_2O; A, $EtOCH_2CH_2OEt$; II, B, Pr_2S; A, $EtSCH_2CH_2SEt$; III, B $(ClCH_2CH_2)_2S$: A, $(ClCH_2CH_2SCH_2-)_2$.

Mixture	B.g.	A, g.	A. %	L_1, mm.	L_2, mm.	L_1/L_2	$L_1/(L_2 - L_1)$	C_A/C_B	$(C_A/C_B)/(L_1/L_2)$
I	0.383	1.697	81.6	231	300	0.770	3.35	4.43	5.70
	.575	1.697	74.7	104	147	.708	2.42	2.95	4.16
	.767	1.697	68.9	293	447	.655	1.90	2.21	3.38
	1.150	1.697	59.6	125	228	.548	1.21	1.48	2.69
II	0.787	1.727	68.8	79	130	.608	1.55	2.19	3.60
	1.113	1.620	59.2	39	76	.513	1.05	1.455	2.84
	1.602	1.044	39.5	70	203	.344	0.526	0.652	1.90
III	0.558	1.290	70.5	73	100	.730	2.70	2.31	3.16
	.885	1.210	57.8	73	111	.657	1.92	1.37	2.08
	1.195	1.021	46.5	37	64	.578	1.37	.854	1.48

other two mixtures mentioned above were treated similarly, the results also being given in Table I. The length (L) of the line on the chart of the continuously recording flow refractometer[7] is proportional to the volume (V) of liquid appearing in the eluent and considerably easier to measure. Thus, $V_1/V_2 = L_1/L_2$, wherein V_1 is the volume at which point the first component is just ready to appear in the effluent liquid, and V_2 the volume of the second component when it is just ready to appear.

In Fig. 2 it will be seen that straight lines are obtained by plotting percentage of the more strongly adsorbed component (A) against L_1/L_2. This, therefore, becomes a simple analytical method for treating such binary mixtures. It is only necessary to obtain the L_1/L_2 value for an unknown and then read off the % A from the curve, previously prepared from knowns.

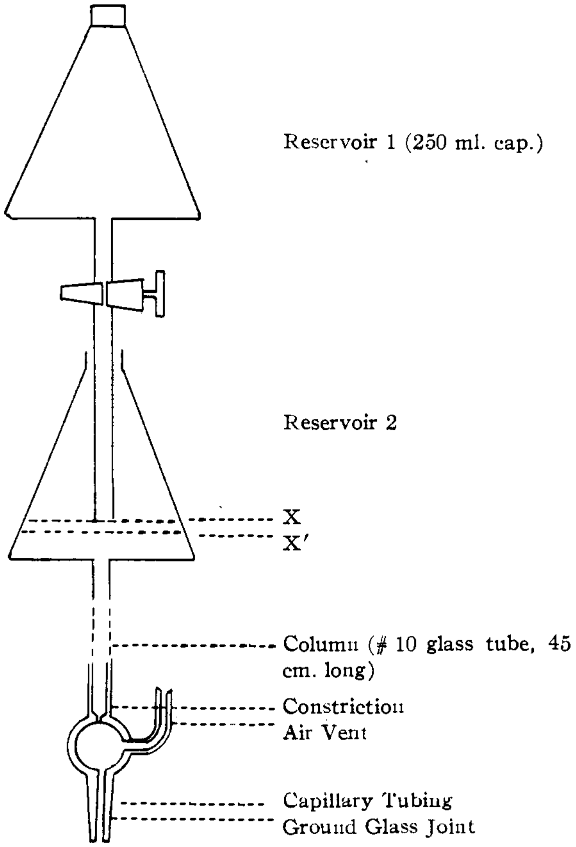

Fig. 1.—The adsorption column and flow rate control.

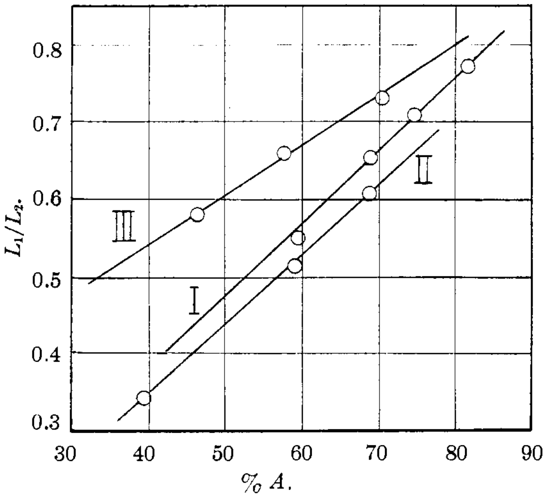

Fig. 2.

The actual curve drawn by the instrument, which plots refractive index of the solution against volume, always showed peculiarities (maxima or minima) at the transition point between components. Three such curves, representing three of the runs of Table I, are presented in Fig. 3. The cause of these irregularities is not known for certain, but probably is due to impurities in the silica gel, such as lignin.[8] They did not interfere with the analysis, however. It was found that L_1 is correctly placed if the distance is measured between the starting point and the point of intersection of these two tangents: the tangent to the plateau and the tangent to the first sharp deviation from the plateau. The distance of L_2 from the starting point is found similarly by the intersection of tangent lines at the end of the next plateau.

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[8] Private communication, Davison Chemical Company.

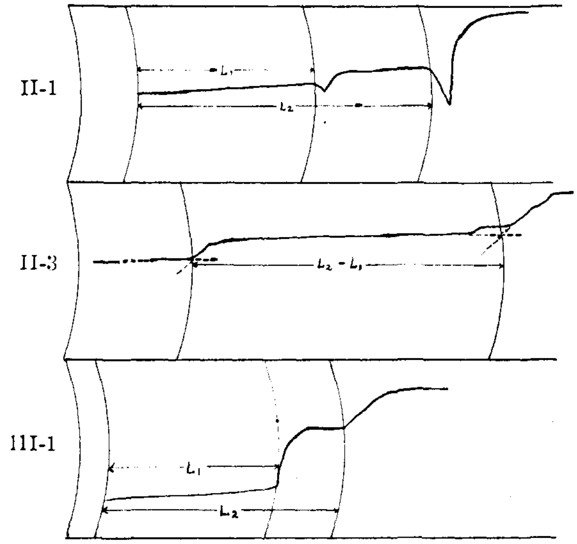

Fig. 3.

The straight-line curves in Fig. 2 make it evident that the percentage of A is linearly related to V_1/V_2 (or L_1/L_2) in the examples cited. This can be derived from equation (1). In the first step $m = 1$. Equation 3 holds when component B is just ready to appear in the effluent.

$$C_{B.1} = 0 - \frac{0 - f_B(C_{B.1}, 0)}{V^0_1} \text{ or}$$

$$C_{B.1} = \frac{f_B(C_{B.1}, 0)}{V^0_1} \qquad (3)$$

In the second step when component A is just ready to appear in the effluent, $m = 2$ and equations 4 and 5 represent components B and A, respectively.

$$C_{B.2} = C_{B.1} - \frac{f_B(C_{B.1}, 0) - f_B(C_{B.2}, C_{A.2})}{V^0_2} \qquad (4)$$

$$C_{A.2} = 0 - \frac{0 - f_A(C_{B.2}, C_{A.2})}{V^0_2} = \frac{f_A(C_{B.2}, C_{A.2})}{V^0_2} \qquad (5)$$

Concentrations $C_{B.2}$ and $C_{A.2}$ in the second step are identical to the C_B and C_A of the unknown. To get a relation between these and V^0_1 and V^0_2, it is necessary to assume a form for the adsorption isotherms f_B and f_A and to eliminate the concentration of B in the first step, *i. e.*, $C_{B.1}$.

Following Claesson, assume Langmuir's adsorption isotherms of the form

$$\left.\begin{aligned} f_B(C_B, C_A) &= \frac{k_B C_B}{1 + l_B C_B + l_A C_A} \\ f_B(C_{B.1}, 0) &= \frac{k_B C_{B.1}}{1 + l_B C_{B.1}} \\ f_A(C_B, C_A) &= \frac{k_A C_A}{1 + l_B C_B + l_A C_A} \end{aligned}\right\} \qquad (6)$$

Substituting (6) in (3), (4) and (5)

$$C_{B.1} = \frac{1}{V_1^0}\left(\frac{k_B C_{B.1}}{1 + l_B C_{B.1}}\right) \qquad (7)$$

$$C_B = C_{B.1} - \frac{\dfrac{k_B C_{B.1}}{1 + l_B C_{B.1}} - \dfrac{k_B C_B}{1 + l_B C_B + l_A C_A}}{V_2^0} \qquad (8)$$

$$C_A = \frac{1}{V_2^0}\left(\frac{k_A C_A}{1 + l_B C_B + l_A C_A}\right) \qquad (9)$$

Now use (7) and (9) to simplify the numerator of (8).

$$C_B = C_{B.1} - \frac{C_{B.1} V_1^0 - \dfrac{k_B}{k_A} C_B V_2^0}{V_2^0} \qquad (10)$$

Solve for $C_{B.1}$ and set into (7).

$$C_{B.1} = C_B \frac{(1 - (k_B/k_A))}{(1 - (V_1^0/V_2^0))}$$

$$\frac{k_B}{V_1^0} = 1 + l_B C_B \frac{(1 - (k_B/k_A))}{(1 - (V_1^0/V_2^0))} \qquad (11)$$

Equations (11) and (9) then become two equations in the two unknowns C_A and C_B. An equation involving the ratio V_2^0/V_1^0 can be obtained by solving (9) for k_A/V_2^0 and dividing into (11). This has the advantage of eliminating the necessity of referring to unit weight of adsorbent, since $V_2^0/V_1^0 = V_2/V_1$ regardless of amount. The result is

$$\frac{k_B}{k_A}\left(\frac{V_2}{V_1}\right) = \frac{1}{1 + l_B C_B + l_A C_A}\left[1 + l_B C_B \frac{(1 - (k_B/k_A))}{(1 - (V_1/V_2))}\right] \qquad (12)$$

Equation 12 becomes greatly simplified if it is assumed that the adsorption of both components in reasonable concentrations is near saturation, *i. e.*, $l_B C_B >> 1$ and $l_A C_A >> 1$, and furthermore if A can displace B or $k_A C_A >> k_B C_B$ and $l_A C_A >> l_B C_B$. Under these conditions equation (12) becomes approximately

$$\frac{k_B}{k_A}\left(\frac{V_2}{V_1}\right) = \frac{l_B C_B}{l_A C_A} \cdot \frac{1}{(1 - (V_1/V_2))} \text{ and}$$

$$\frac{V_1}{V_2} = \frac{C_A}{C_A + \dfrac{k_A l_B}{k_B l_A} C_B} \qquad (13)$$

Furthermore, if $k_A/l_A = k_B/l_B$, (eq. 14) which means that the saturation adsorption in any desired units would be the same for each component, then (13) reduces to (15)

$$\frac{V_1}{V_2} = \frac{C_A}{C_A + C_B} \qquad (15)$$

In other words, the mole percentage or the weight percentage of A would be proportional to V_1/V_2, depending on the units used in (14). The fact that the lines of Fig. 2 do not pass through the origin suggests that certain of the assumptions made above are too crude.

A more accurate treatment of results would be expected if the assumption in equation (14) is not made. Let

$$k_A l_B / k_B l_A = p$$

where p is an undetermined constant and represents the ratio of the saturation adsorptions of A and of B. Equation (13) can be rearranged into

$$\frac{C_A V_2}{C_B V_1} = \frac{C_A}{C_B} + p \qquad (16)$$

Figure 4 shows a plot of the left side of (16) *versus* C_A/C_B. In accordance with the equation straight

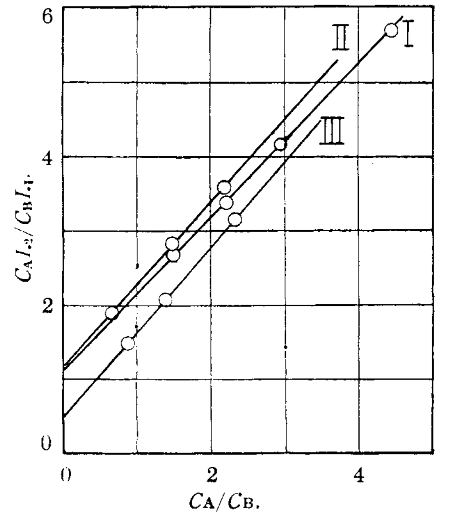

Fig. 4.

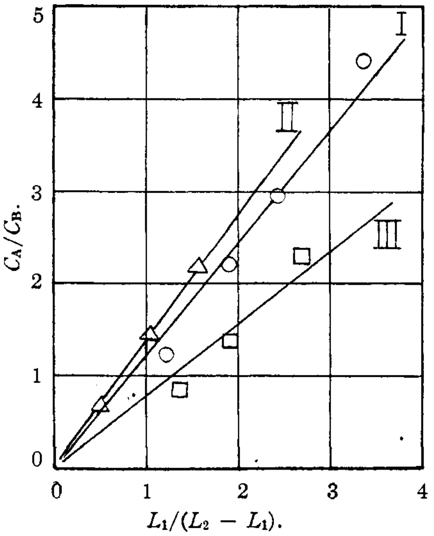

Fig. 5.

lines result but with slopes deviating slightly from the expected value one, being 1.03, 1.11, and 1.16 for I, II, III, respectively. The intercepts give values of p for the different systems:. 1.12, 1.17, 0.48 for I, II, III.

For purposes of analytical work, equation (17) is a more convenient rearrangement of (16)

$$\frac{C_A}{C_B} = p\left(\frac{V_1}{V_2 - V_1}\right) \quad (17)$$

Figure 5 shows the plot of C_A/C_B *versus* $V_1/(V_2 - V_1)$ or its equivalent, $L_1/(L_2 - L_1)$. Case III does not follow a straight line, through the origin probably because of the large slope in Fig. 4. Values of p calculated from the slopes in Fig. 5 are found to be higher (1.21, 1.39, 0.78 for I, II, III) than those obtained as intercepts in Fig. 4. For analyses a plot such as Fig. 5 would be useful especially if a calibration curve on a set of knowns is first constructed.

Summary

The method of frontal analysis has been extended and applied to the problem of analyzing various mixtures of ethers and sulfides.

EVANSTON, ILLINOIS RECEIVED SEPTEMBER 10, 1949

[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Decomposition of Benzoyl Peroxide in the Presence of Iodine. I. Aromatic Solvents[1]

BY GEORGE S. HAMMOND

The mechanism of the decomposition of benzoyl peroxide has been studied extensively during the last twenty-five years.[2] The complexity of the process is indicated by the extreme variation in the rate of decomposition in different solvents and at different concentrations in the same solvent.[3] Nozaki and Bartlett have discussed the kinetics in detail and show that the variation in rate may be largely attributed to the ability of radicals, formed either in the primary process or by the reactions of the primary products with solvent, to attack peroxide and destroy it in a chain reaction.

In a solvent in which nearly all of the peroxide is destroyed by this induced reaction it is an easy matter to formulate the propagation reactions from a knowledge of the products formed. This has been done by Cass[4] for decomposition in ether. It is more difficult to account for the products in solvents such as benzene in which both the spontaneous and chain reactions are important. It is of interest to attempt a more complete elucidation of the mechanism in these instances because diacyl peroxides as a class constitute one of the best sources of reactive free radicals at relatively low temperatures.[5] In particular it is important to know whether or not the radical R· is produced in the decomposition of $(RCO_2)_2$ by the loss of carbon dioxide either in the primary process or by

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(1) We gratefully acknowledge the finanical support of this research by the Office of Naval Research.

(2) For references to the older literature, see McClure, Robertson, and Cuthbertson, *Can. J. Research*, **20B**, 103 (1942).

(3) (a) Brown, THIS JOURNAL, **62**, 2657 (1940); (b) Nozaki and Bartlett, *ibid.*, **68**, 1686 (1946); (c) **69**, 2299 (1947).

(4) Cass, *ibid.*, **68**, 1976 (1946).

(5) For example see Kharasch, *et al.*, *J. Org. Chem.*, **14**, 91 (1949), and earlier papers in the series.