tilled separately in a small Claisen flask and boiled at the same temperature. The sweet smelling alcohol had the constants: b. p. 80–81° (6.0 mm.); d^{27}_4 0.826; $n^{24.5}_D$ 1.4340; M_D (calcd.) 49.9; M_D (found) 49.7.

Anal. Calcd. for $C_{10}H_{24}O$: C, 75.88; H, 14.01. Found: C, 75.9; H, 13.9.

Attempted Condensation of 2-Ethyl-2-hexenal with 4-Heptanone.—The procedure was the same as that used in the butanal and 4-heptanone condensation except that stirring was continued for three days after all of the 2-ethyl-2-hexenal had been added. Two and one-half moles (315 g.) of 2-ethyl-2-hexenal and 8 moles (892 g.) of 4-heptanone were used. After removal of the unreacted aldehyde and ketone the following fractions were obtained: (1) b. p. 87–88° (9.5 mm.), 25 cc. (2.5%) of 5-ethyl-5-nonen-4-one; (2) b. p. 124–126° (14 mm.), 20 cc. (1.6% of 5-ethyl-6-hydroxy-4-nonanone; (3) b. p. above 170° (20 mm.), tarry residue.

Fraction 1 appears to be the same unsaturated ketone obtained in the butanal and 4-heptanone condensation. The following properties may be compared with those given above for 5-ethyl-5-nonen-4-one: b. p. 87–88° (9.5 mm.); n^{23}_D 1.4496; m. p. of semicarbazone 118–119° (melting point of mixed semicarbazones 112–114°); anal. semicarbazone: C, 63.1; H, 10.5. The melting point of the mixed semicarbazones was always lowered 5–6° despite repeated recrystallizations. No explanation for this fact can be given except that a small amount of impurity may be present in one or both of the derivatives. On quantitative hydrogenation a sample of the 5-ethyl-5-nonen-4-one from this condensation absorbed 1.27 mole-equivalent of hydrogen.

Fraction 2 appears to be identical with the ketol obtained in the butanal and 4-heptanone condensation. Its physical properties may be compared with those given above for 5-ethyl-6-hydroxy-4-nonanone; b. p. 118–119° (18 mm.); d^{21}_4 0.927. Dehydration of the ketol by heating with iodine at atmospheric pressure gave 5-ethyl-5-nonen-4-one, b. p. 90–93° (11 mm.), and water.

Summary

Butanal has been condensed with 4-heptanone and 3-hexanone in the presence of alkali and the mono-condensation products were isolated in small yields and identified in each case. With 4-heptanone, condensation occurs on the methylene group; with 3-hexanone, condensation occurs on the α-carbon of the ethyl group.

An attempt was made to condense 2-ethyl-2-hexenal with 4-heptanone, but the unsaturated aldehyde hydrates in the alkaline medium forming *n*-butyraldol, which dealdolizes to form butanal. The butanal formed then reacts with the 4-heptanone giving the same unsaturated ketone and ketol isolated in the 4-heptanone and butanal condensation.

SEATTLE, WASHINGTON

RECEIVED MARCH 6, 1948

[CONTRIBUTION FROM THE HALL LABORATORY OF CHEMISTRY OF WESLEYAN UNIVERSITY]

The Use of Fluorescent Silica Gel Mixtures in the Chromatography of Colorless Compounds[1]

BY JOHN W. SEASE

Brockmann and Volpers[2] and Sease[3] have shown that the development of chromatograms of certain colorless, non-fluorescing compounds may be observed visually, provided that specially prepared fluorescent adsorbents are employed and the chromatographic column is illuminated with ultraviolet light. Brockman and Volpers prepared their adsorbents by adsorbing fluorescent organic materials on the adsorbent, while Sease obtained fluorescent silica gel by mixing 2.5% of a fluorescent zinc sulfide with silica. The use of this latter adsorbent was limited by the characteristics of the zinc sulfide to those compounds which exhibited appreciable absorption in the region 330–390 mμ. The present work, undertaken to determine the feasibility of extending the range by employing a fluorescent material sensitive to wave lengths below 330 mμ, shows that this may be achieved by admixture of a zinc silicate whose practical excitation range is approximately 230–290 mμ. By practical excitation range is meant the usable range when the adsorbent–fluorescent material mixture is packed in a chromatographic tube and wet with petroleum ether. Inclusion of both this zinc silicate and the zinc sulfide used in earlier work[3] gives a mixture whose excitation range is continuous from 390–230 mμ.

On such an adsorbent, containing 2.5% of each fluorescent material, 40 binary mixtures involving 25 different compounds have been chromatographed. Detailed descriptions of the resulting separations are given in Table I. Satisfactory visibility of the adsorbed compounds was obtained in every case by illuminating the column with the hydrogen lamp from a Beckman Spectrophotometer, which provides continuous illumination to below 220 mμ. A Purple X bulb (General Electric Co.) was usable in some cases, but not in others, where the spectral absorption of the zones occurred at very low wave lengths. Zones visible with either light source were almost invariably seen more readily with the hydrogen lamp. Because of the discontinuous nature of the radiation afforded, a quartz mercury lamp was of little value; a few compounds gave excellent shadows, but most were invisible.

Acetone was employed in preliminary experiments as an additive agent for increasing the strength of the petroleum ether developer, but was discarded in favor of diethyl ether when the latter was found to be markedly superior in producing certain separations. Benzene was not

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[1] This paper was presented before the Division of Analytical and Micro Chemistry at the 113th Meeting of the American Chemical Society, Chicago, April, 1948.

[2] H. Brockmann and F. Volpers, *Ber.*, **80**, 77 (1947).

[3] J. W. Sease, THIS JOURNAL, **69**, 2242 (1947).

TABLE I

SEPARATIONS OF PAIRS OF COMPOUNDS ON EIMER AND AMEND SILICA COLUMNS MADE FLUORESCENT BY ADDITION OF FLUORESCENT ZINC SILICATE

Pair no.	Compound A	Mg.	Compound B	Mg.	Devel.[a] ml.	Zones,[m] mm.				
						I	II	III	IV	V
1	*m*-Nitrobenzaldehyde	16	Anisaldehyde	14	600^{i}	210	30	10	40	100
2	*m*-Nitrobenzaldehyde	16	*o*-Nitrobenzaldehyde	16	250^{i}	90	20	20	30	30
3	*m*-Nitrobenzaldehyde	14	Cinnamaldehyde	13	200^{i}	60	40	20	30	50
4	Anisaldehyde	14	*o*-Nitrobenzaldehyde	16	500^{i}	250	30	20	30	50
5	Anisaldehyde	14	Cinnamaldehyde	13	250^{i}	120	30	20	30	30
6	Anisaldehyde	14	Benzaldehyde	16	100^{f}	5	5	30	20	100
7	*o*-Nitrobenzaldehyde	13	Cinnamaldehyde	13	400^{i}	250	50	20	35	70
8	*o*-Nitrobenzaldehyde	13	Xanthone	14	500^{h}	250	60	50	40	10
9	Cinnamaldehyde	16	Xanthone	12	500^{i}	320	60	30	..	...
10	Cinnamaldehyde	13	Acetophenone	13	125^{h}	70	20	10	30	50
11	Cinnamaldehyde	12	Benzaldehyde	16	100^{g}	25	25	50	20	80
12	Xanthone	14	Acetophenone	15	200^{g}	70	15	20	30	50
13	Acetophenone	12	Phenacyl bromide	12	90^{i}	130	30	10	20	40
14	Acetophenone	15	Benzophenone	10	100^{g}	55	25	20	35	70
15	Phenacyl bromide	9	Benzaldehyde	12	350^{g}	330	50	30	..	...
16	Phenacyl bromide	12	Benzophenone	13	600^{f}	255	70	80	..	...
17	Phenacyl bromide	15	Salicylaldehyde	14	100^{f}	40	25	10	30	60
18	Benzaldehyde	12	Benzophenone	13	320^{g}	300	30	10	30	20
19	Benzaldehyde	16	Salicylaldehyde	14	200^{f}	90	25	15	30	20
20	Benzophenone	12	Salicylaldehyde	14	100^{f}	90	30	25	30	20
21	Dimethyl phthalate	15	Di-*n*-butyl phthalate	13	100^{f}	20	20	20	20	80
22	Di-*n*-butyl phthalate	18	Phenyl acetate	14	100^{f}	10	10	20	10	90
23	Phenyl acetate	14	Methyl benzoate	17	100^{f}	50	15	15	20	90
24	Phenyl acetate	14	Phenyl benzoate	15	100^{f}	50	10	20	20	60
25	Methyl benzoate	13	Phenyl benzoate	13	375^{f}	300	20	20	30	20
26	Pyridine	17	*p*-Chloroaniline	18	200^{g}	5	5	10	10	120
27	Pyridine	17	*p*-Toluidine	9	200^{g}	5	5	15	15	75
28	Pyridine	17	Aniline	17	200^{g}	5	7	15	20	100
29	*p*-Chloroaniline	16	*p*-Toluidine	13	900^{j}	250	35	7	20	75
30	*p*-Chloroaniline	16	Aniline	24	525^{k}	260	70	10	45	30
31	*p*-Chloroaniline	18	*o*-Toluidine	14	300^{i}	50	20	30	20	70
32	*p*-Toluidine	13	Aniline	14	500^{k}	240	50	30	..	...
33	*p*-Toluidine	11	*o*-Toluidine	14	300^{i}	50	25	20	35	80
34	Aniline	15	*o*-Toluidine	13	225^{f}	100	30	10	20	20
35	Aniline	17	Dimethylaniline	16	70^{i}	10	10	110	30	20
36	*o*-Toluidine	14	Dimethylaniline	16	50^{i}	10	5	75	40	60
37	*o*-Nitrobenzaldehyde	14	*p*-Nitrobenzyl bromide	12	40^{e}	10	10	15	15	115
38	*p*-Nitrobenzyl bromide	12	*o*-Nitrochlorobenzene	15	100^{b}	10	30	10	30	70
39	*o*-Nitrochlorobenzene	17	Nitrobenzene	19	200^{c}					
					300^{d}	170	100	40	..	...
40	Nitrobenzene	19	*p*-Nitrotoluene	15	300^{d}	320	65	50	..	...

[a] The ether content of the various developers is denoted by the following superscripts: ^{b} 0%; ^{c} 0.25%; ^{d} 0.5%; ^{e} 1%; ^{f} 2%; ^{g} 5%; ^{h} 7.5%; ^{i} 10%; ^{j} 15%; ^{k} 20%. [m] Each chromatogram is described in terms of the following zones, whose thicknesses in mm. are given by the numbers under the corresponding Roman numerals: I, fluorescent (empty) section; II, shadow (upper zone, Compound A or mixture of Compounds A and B in case zones IV and V were not obtained); III, fluorescent (empty) section; IV, shadow (lower zone, Compound B); V, fluorescent (empty) section.

tried as a developing agent, since Skellysolve B (60–70°) and Skellysolve C (86–100°), both of which presumably contain small amounts of benzene, cause shadows on the column.

The relative strengths of adsorption for those pairs which gave only partial separations are so nearly alike that, although results under carefully controlled conditions are reproducible, slight variations in adsorbent strength or developer may cause inversions. For example, nitrobenzene is above *p*-nitrotoluene on Eimer and Amend silicic acid but below it on Merck silicic acid.

A considerable number of experiments was carried out using Merck Reagent silicic acid diluted with 50% Celite 535. The incorporation of the opaque filter aid makes the fluorescence quite weak, unless the concentration of fluorescent material is increased beyond 2.5%, which would be advisable in future work. As a general rule, the Merck adsorbent gave more diffuse zones than the Eimer and Amend product and separations were poorer or failed entirely.

Recovery of both fluorescent silica gels was undertaken to conserve the limited supply of adsorbents. No deterioration has been observed even after repeated use, although, if the zinc sulfide fluorescence is to be utilized, care must be exercised to ensure that the zinc sulfide particles remain uniformly dispersed. The recovered material is a distinctly weaker adsorbent than fresh silicic acid and minor variations have been noted in the strength of various recovered batches. The weaker adsorptive properties of the recovered silicic acid have been an advantage in the present work, since they permitted several separations which could not be attained on fresh silica gel.

Acknowledgment.—The author would like to express his appreciation to Mary L. Sease who assisted in carrying out the experiments, and to Dr. Frank Swindells and Dr. Emery Meschter of the Photo Products Department of the du Pont Co. for their kindness in making available the fluorescent materials used in this work.

Experimental

Silicic acid (Merck Reagent, diluted with 50% Celite 535, or Eimer and Amend, C. P., undiluted) was mixed thoroughly with 2.5% of No. 62 zinc sulfide[4] and 2.5% of No. 609 zinc silicate[4] and packed in a quartz chromatographic tube of 2.2 cm. inner diameter; 5–10 ml. of petroleum ether (Skellysolve F, b. p. 35–60°) solution containing the two substances to be separated was poured on the column, which was then developed with petroleum ether containing 0–20% of USP diethyl ether. Movement of the zones was observed by illuminating the column in a darkened room with ultraviolet light from a hydrogen lamp detached from a Beckman Spectrophotometer.

At the conclusion of development each shadowed zone was isolated mechanically and dried in the air for one-half to twelve hours. Elution with 50–75 ml. of 96% ethanol gave a solution whose qualitative and quantitative composition could easily be determined on a Beckman Spectrophotometer. In those experiments where no apparent separation had occurred, the top and bottom thirds of the shadowed zone were separated, eluted with alcohol and analyzed spectroscopically, the middle third being discarded. In the one case where the two separated compounds had the same spectral absorption (dimethyl phthalate and dibutyl phthalate) the zones were eluted with 30–40 ml. of diethyl ether, the ether was evaporated off, and the residue, after purification by fractional distillation according to the technique of Morton and Mahoney,[5] was identified by its boiling point.

Fresh adsorbent was prepared for use and used adsorbent was recovered by washing in a large chromatographic tube with 3 *V* of 96% ethanol (*V* is that volume of liquid required to wet the silicic acid[6]), next with 1 *V* of diethyl ether, and finally with 3 *V* of petroleum ether. The extruded adsorbent was dried for a few minutes in the air and then for at least eight hours in a desiccator evacuated continuously by a mechanical oil pump.

Summary

A mixture of silica gel with fluorescent zinc silicate and zinc sulfide has been found to be much superior to the silica gel–zinc sulfide mixture used in earlier work on the chromatography of colorless compounds, from the standpoint of both ease of visibility and number of compounds visible. Forty separations involving twenty-five compounds are described and adsorption sequences are given.

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(4) Obtained from the Photo Products Division, E. I. du Pont de Nemours and Co., Inc., Towanda, Penna.

(5) A. A. Morton and J. F. Mahoney, *Ind. Eng. Chem., Anal. Ed.* **13**, 494 (1941).

(6) W. A. Schroeder, *Ann. N. Y. Acad. Sci.*, **XLIX**, 204 (1948).

MIDDLETOWN, CONN. RECEIVED JUNE 16, 1948

[CONTRIBUTION FROM GULF RESEARCH & DEVELOPMENT COMPANY'S MULTIPLE FELLOWSHIP, MELLON INSTITUTE]

Some Mechanism Studies on the Fischer–Tropsch Synthesis Using C^{14}

BY J. T. KUMMER, T. W. DEWITT AND P. H. EMMETT

Fischer[1] and his co-workers have suggested that the metallic carbide is an intermediate in the synthesis of hydrocarbons from carbon monoxide and hydrogen over the catalysts iron, nickel and cobalt. This theory has also been accepted by numerous later writers. The use of the recently available radioactive carbon isotope, C^{14}, as a tracer seemed to provide a possible direct method for testing this hypothesis. Accordingly, the experiments described in this paper were undertaken. We have attempted to determine whether the mechanism of hydrocarbon synthesis over iron and cobalt catalysts is the formation of a carbide by the reaction of carbon monoxide with the metal catalyst followed by the reduction of the surface of this carbide to methylene groups which combine to form hydrocarbons; or whether, on the other hand, the mechanism is such that the hydrocarbons are formed by some adsorption mechanism that does not involve the carbide as an intermediate.

The general plan of the experiments was quite simple. If the carbide is an intermediate, a surface layer of metal carbide containing radioactive C^{14} should cause the initial hydrocarbon products formed by exposing a mixture of hydrogen and normal carbon monoxide to the radioactive carbide at synthesis conditions to be approximately as radioactive as the surface. Similarly, a surface carbided with non-radioactive carbon monoxide should, on contact with a H_2–$C^{14}O$ mixture, at first form hydrocarbons with much lower radioactivity than that of the H_2–$C^{14}O$ mixture. Before the synthesis experiments could be carried out, however, it was necessary to prepare a surface containing C^{14} as metal carbide, and to determine whether the *exchange* of the carbon in carbon monoxide and in other hydrocarbons with the carbon

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(1) Fischer and Tropsch, *Ges. Abhandl. Kenntnis Kohle*, **10**, 313 (1932).