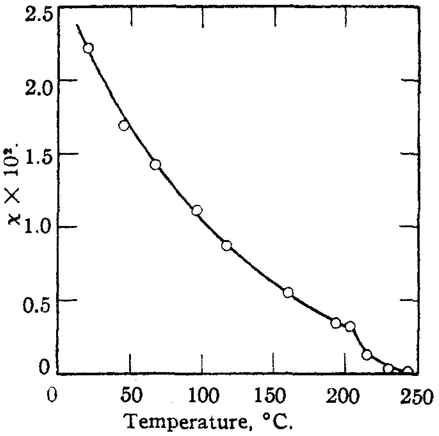

Fig. 10.—Magnetization and Curie point of a catalyst derived from nickel ammonium molybdate.

Summary

Magnetic susceptibility measurements, over a range of temperature and field strength, have been made on a series of nickel-activated copper hydrogenation catalysts, on nickel supported on magnesia, and on a catalyst derived from ammonium nickel molybdate.

Active copper–nickel catalysts consist of a continuous series of solid solutions ranging in composition from about 66 to 92.5% nickel. Pure metallic nickel is not present.

Thermal deactivation is accompanied by diffusion of copper into the nickel-rich alloys.

Thermal deactivation of nickel supported on magnesia must proceed by a different mechanism because, while the magnetization is lowered, the Curie point remains the same.

Poisoning experiments indicate that the poisons affect a small but measurable fraction of the nickel atoms, presumably those on the surface of the active microcrystals. It may be conjectured from this that the active microcrystals are approximately codimensional with the ultimate ferromagnetic domain.

The catalyst derived by heating and reducing ammonium nickel molybdate contains no metallic nickel.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA]

Alkyl *p*-Nitrobenzoates[1]

BY MARVIN D. ARMSTRONG AND J. E. COPENHAVER

Henstock[2] has suggested the use of the alkyl *p*-nitrobenzoates as derivatives for use in the identification of alcohols and has prepared the first six members of the series. The purpose of this investigation was to extend this series and to study the physical properties of these compounds.

The esters were prepared by refluxing an excess of the lower alcohols with the acid chloride and by heating the higher alcohols with a 10% excess of *p*-nitrobenzoyl chloride. The reaction proceeded rapidly with the alcohols through the butyl but it was necessary to heat the others for two hours or longer to carry the reaction to completion. The crude esters were dissolved in ether and washed with a 10% sodium carbonate solution until free from nitrobenzoic acid. The ethereal solution was then washed with water, the ether evaporated and the esters recrystallized from petroleum ether, usually two or three times, until they showed constant melting points. The liquid esters, amyl through nonyl, were rapidly distilled *in vacuo* until a constant index of refraction was secured (see Table I) and in general a yield of 70–90% was obtained. The melting points of the esters with analytical data for nitrogen are given in Table II and are plotted in Fig. 1.

TABLE I

PHYSICAL PROPERTIES OF THE LIQUID *p*-NITROBENZOATES

Ester	B. p., °C.	*P*, mm.	n^{20}_D	d^{20}_{20}
Amyl	144–146	3	1.5186	1.1452
Hexyl	175–177	8	1.5153	1.1193
Heptyl	147–155	5	1.5122	1.0973
Octyl	170–175	5	1.5094	1.0817
Nonyl	175–185	5	1.5074	1.0719

The esters are light yellow through nonyl; from decyl through eicosyl, white crystalline solids. From Fig. 1 it can be seen that, beginning with the hexyl ester, the melting points exhibit regular alternation, the esters containing an even number of carbon atoms in the alkyl group having the higher melting points. The lower members exhibit a very irregular melting point pattern.

The *p*-nitrobenzoates may be used for the identification of the aliphatic alcohols except for the few which have melting points too close together. They are easily prepared and purified, and melt sharply.

The melting points were taken, with mechanical stirring in a 200-cc. bulb, fitted with a side-arm for the thermometer and melting point tube. Standard Anschütz thermometers were used.

The authors wish to express their appreciation to Dr. E. Emmet Reid, Research Advisor, University of South Carolina, for suggesting this problem and for his valuable aid during its

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(1) Original manuscript received July 17, 1941.

(2) Herbert Henstock, *J. Chem. Soc.*, 216 (1933).

TABLE II

MELTING POINTS AND ANALYSES OF THE *p*-NITROBENZOATES

Ester	M. p., °C. (cor.)	Nitrogen, % Calcd.	Found
Methyl	95.1[a]	7.73	8.03
Ethyl	56.3	7.18	7.14
n-Propyl	34.0	6.70	7.12
i-Propyl	108.3	6.70	6.71
n-Butyl	35.3	6.28	6.56
i-Butyl	69.5	6.28	6.58
s-Butyl	25.0	..	..
Amyl	11.2	5.91	6.09
Hexyl	6.7	5.59	5.78
Heptyl	7.9	5.28	5.36
Octyl	16.6	5.02	5.10
Nonyl	18.7	4.78	4.87
Decyl	29.8[b]	4.56	4.52
Undecyl	29.2	4.36	4.86
Dodecyl	41.9	4.18	4.17
Tridecyl	37.4	4.01	3.97
Tetradecyl	51.2	3.86	4.06
Pentadecyl	45.8	3.71	3.75
Hexadecyl	58.4	3.58	3.79
Heptadecyl	53.8	3.46	3.40
Octadecyl	64.3	3.36	3.46
Nonadecyl	58.9	3.23	3.29
Eicosyl	69.4	3.15	3.20

[a] Henstock, *J. Chem. Soc.*, 216 (1933), gave melting points for the following esters: methyl 96°, ethyl 57°, *n*-propyl 32°, *i*-propyl 55.5°, *n*-butyl 35°, *i*-butyl 67°, amyl 54°; Wilbrand and Beilstein, *Ann.*, 128, 262–263 (1863), gave the same values as Henstock for methyl and ethyl; *Chem. Zentr.* 80, (II) 1025 (1909), gave 35° for propyl; R. Kuhn, *et al.*, *Ber.*, 75B, 711–719 (1942), gave butyl 34–35°, dodecyl 43–44° and hexadecyl 53–55°. [b] Komppa and Talvitie, *J. prakt. Chem.*, 135, 193 (1932), gave 30.2° for decyl.

completion. The alcohols from decyl through octadecyl were from those prepared by Meyer and Reid.[3] Thanks are also due Hooker Electrochemical Company for furnishing the *p*-nitrobenzoyl chloride.

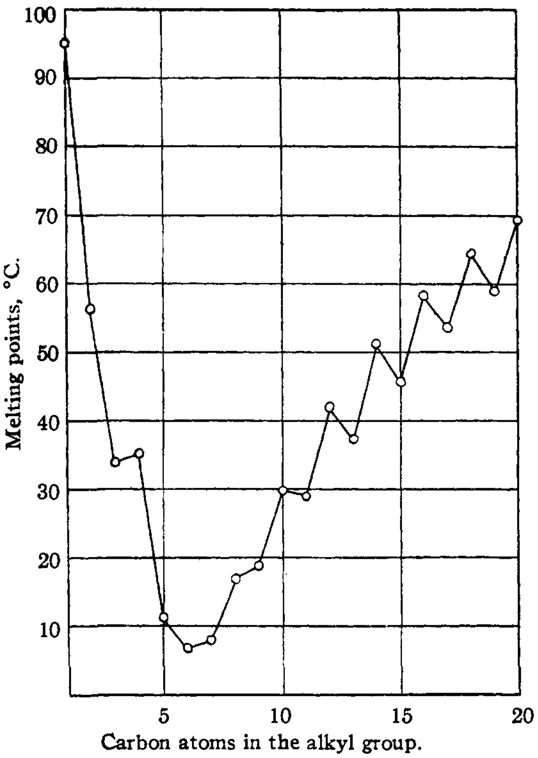

Fig. 1.—Melting points of the alkyl *p*-nitrobenzoates.

Summary

The alkyl esters, through eicosyl, of *p*-nitrobenzoic acid have been prepared and some of their properties determined. A curve is shown for the melting points, which exhibits regular alternation above the hexyl ester. Fifteen of the twenty-three derivatives are new compounds.

COLUMBIA, SOUTH CAROLINA RECEIVED AUGUST 7, 1943

[3] Meyer and Reid, THIS JOURNAL, 55, 1574–1584 (1933).

NOTES

The Dissociation of Dimethyl Ether-Boron Trifluoride at Low Temperatures

BY HERBERT C. BROWN AND[1a] RICHARD M. ADAMS

There has appeared recently an electron diffraction study of dimethyl ether-boron trifluoride,[1] the results of which are of considerable importance to chemists interested in the properties of addition compounds. Before the interpretation of the electron diffraction photographs is accepted, however, one doubtful point should be clarified. In the article cited, the authors state that the dissociation of dimethyl ether-boron trifluoride in the vapor phase at 40° is less than 10%, and may be neglected in the interpretation of the diffraction patterns. There is, however, good reason to believe that the dissociation of the complex is much greater than the figure given. This opinion is based upon the following evidence.

Two independent studies of the vapor phase dissociation of dimethyl ether-boron trifluoride are now available. One by Laubengayer and Finlay[2] was published simultaneously with the

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[1] Bauer, Finlay and Laubengayer, THIS JOURNAL, 65, 889 (1943).

[2] Laubengayer and Finlay, *ibid.*, 65, 887 (1943).