

TABLE II
MELTING POINTS AND ANALYSES OF THE *p*-NITRO-
BENZOATES

Ester	M. p., °C. (cor.)	Nitrogen, %	
		Calcd.	Found
Methyl	95.1 ^a	7.73	8.03
Ethyl	56.3	7.18	7.14
<i>n</i> -Propyl	34.0	6.70	7.12
<i>i</i> -Propyl	108.3	6.70	6.71
<i>n</i> -Butyl	35.3	6.28	6.56
<i>i</i> -Butyl	69.5	6.28	6.58
<i>s</i> -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 Electro-

(3) Meyer and Reid, *THIS JOURNAL*, 55, 1574-1584 (1933).

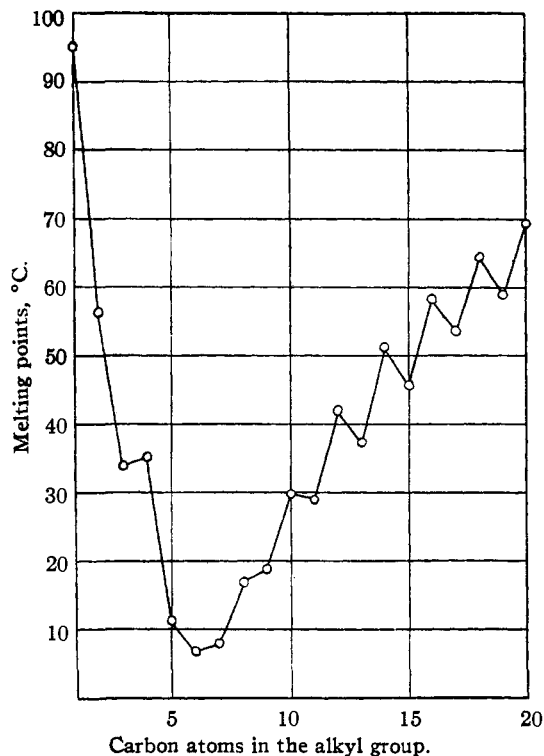


Fig. 1.—Melting points of the alkyl *p*-nitrobenzoates.

chemical Company for furnishing the *p*-nitrobenzoyl chloride.

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

NOTES

The Dissociation of Dimethyl Ether-Boron Trifluoride at Low Temperatures

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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, how-

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

ever, 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 Finlay² was published simultaneously with the

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

electron diffraction study; another by the present authors,³ appeared some six months earlier. In the latter paper the dissociation constants of the complex over the temperature range from 66 to 99° are given. These constants were satisfactorily represented by the equation

$$\log K_p = -2904/T + 7.049 \quad (1)$$

The heat of dissociation, calculated from the variation of the dissociation constant with temperature, was 13.3 kcal.

Laubengayer and Finlay list two series of measurements, one covering the temperature range from 90 to 130°, and the other the range from 50 to 100°. Their heat of dissociation, calculated from the dissociation constants in the range from 100 to 130°, was 13 kcal., in excellent agreement with the one found by the present authors. Moreover, the dissociation constants in the range from 100 to 130° agree satisfactorily with the ones calculated for the same temperatures by means of our equation (1) (Table I). On the other hand, Laubengayer and Finlay's measurements at lower temperatures are in marked dis-

agreement with our experimental values in the same temperature range. Moreover, their results are not self-consistent—for example, their recorded values for the dissociation constants at 80, 90 and 100° are 0.107, 0.055 and 0.180, respectively (Table I); and their value for 50°, 0.002, is obviously far too low. The difficulty of reconciling these measurements at lower temperatures either with their own results at the higher temperatures or with our data is well brought out by Fig. 1. It therefore appears reasonable to discard the few erratic values (90, 80, 50°) in calculating the value of the dissociation constant at 40°, and to rely for this purpose primarily on equation (1), which fits the data quite satisfactorily from 130 to 66°.

TABLE I
DISSOCIATION DATA FOR DIMETHYL ETHER-BORON TRIFLUORIDE

Source of data	Temp., °C.	Dissociation constant, $K_{(atm.)}$	
		Found	Calcd.
B. and A. ³	66	0.032	0.030
	70	.038	.038
	73	.044	.045
	75.5	.051	.052
	78.5	.067	.061
	81	.071	.070
	83.5	.079	.080
	86	.091	.091
	89	.111	.107
	93	.131	.130
L. and F. ¹ (Sample No. 1)	99	.171	.175
	90	.055	.112
	100	.180	.183
	110	.312	.293
	120	.483	.458
L. and F. ² (Sample No. 2)	130	.701	.699
	50	.002	.011
	60	.020	.021
	80	.107	.066
	100	.180	.183

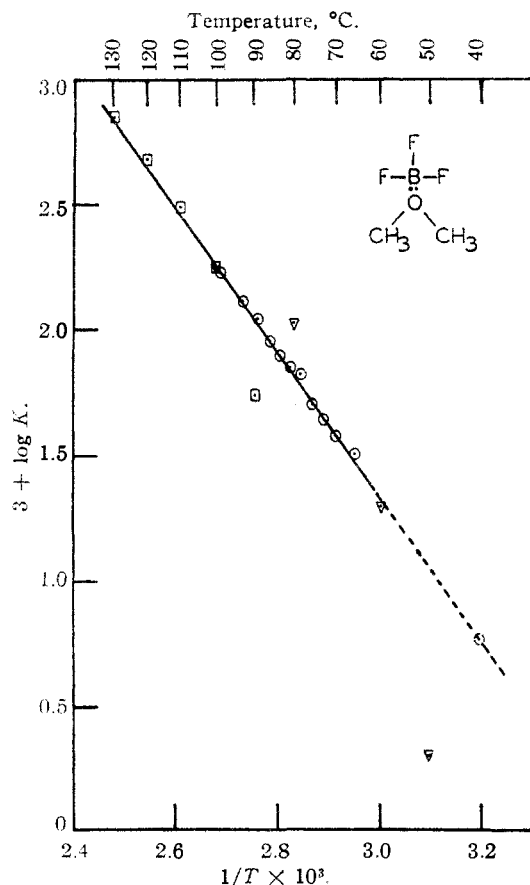


Fig. 1.—Dissociation data of dimethyl ether-boron fluoride: □, data of L. and F.² (sample 1); ▽, data of L. and F.² (sample 2); ○, data of B. and A.³

(3) Brown and Adams, *THIS JOURNAL*, **64**, 2559 (1942).

Bauer, Finlay and Laubengayer¹ do not report the basis of their conclusion that the dissociation of dimethyl ether-boron trifluoride is less than 10% at 40°. The dissociation constant at 40°, calculated by equation (1), is 0.0059; at this temperature and at the saturation pressure, 9.5 mm., the complex is 57% dissociated. At pressures below the saturation pressure, the degree of dissociation is, of course, even greater. The conclusions drawn from the electron diffraction photographs should be reconsidered in the light of these facts.⁴

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RECEIVED JUNE 22, 1943

(4) Before this Note was submitted to the *JOURNAL*, a copy was sent to Drs. Laubengayer and Bauer. Dr. Bauer has informed us that a reexamination of the electron diffraction study will be made in order to determine the effect of the high dissociation of the complex on the interpretation of the diffraction photographs.